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JANUARY, 1910.

No. 1

## EDITORIALS.

### THE NEW YORK CHEMISTS' BUILDING.

A most significant event in the annals of American chemical development is the incorporation of the Chemists' Building Company, of New York City. Enterprising New York chemists have had the matter under consideration for some time and the plans, as now put forward, indicate a wealth of detail and carefully thought-out plans, worthy of highest respect and general support. *The Percolator*, the bulletin of the New York Chemists' Club, for November 15th makes the following statement:

"The incorporation of the Chemists' Building Company is now complete, the incorporators being Messrs. Baekeland, Bogert, Coblentz, Elliott, Hasslacher, McMurtrie, Plaut, Baskerville, Chandler, Doremus, Falk, Loeb, Nichols, Jr., I. F. Stone, Toch.

"At a meeting held on Friday, November 12th, the following directors were chosen:

"Morris Loeb, *President*; Charles F. Chandler, *Vice-President*; Albert Plaut, *Treasurer*; W. H. Nichols, Jr., *Secretary*; Leo H. Baekeland office.

"The architects are busy with the plans of the building, and it is hoped that estimates can be obtained

shortly. The Finance Committee, on the other hand, is still lacking about \$30,000 in subscriptions before the directors will be warranted in declaring the plan operative, and it is the duty of all those interested in the project to lighten the arduous labors of this committee.

"While the Chemists' Club will profit largely by the erection of this building, the fact cannot be emphasized too strongly that all the chemists of the United States will be benefited to an equal degree, not merely those residing in and about New York. Non-residents will find it a very suitable stopping place during their occasional visits to the city, and particularly convenient by reason of the library and other professional conveniences which this building will contain. This library in itself will be made so complete that it will be the natural bureau of information for all members of our various chemical societies, and the museum, if the present plans are carried out, will perform for chemistry the services which the Smithsonian Institution renders to natural history. The individual laboratories will frequently enable the temporary resident of New York to perform the experiments essential to the progress of his work, as well as affording commercial and research chemists, resident in the city, but not attached to any particular institutions or corporations, an opportunity to carry out their work economically and expeditiously.

"Our members have, therefore, every incentive to subscribe themselves, and to urge such companies or individuals to contribute to its funds, who owe their own business success, in a large measure, to the advance of chemical science.

"To eliminate all possible misunderstanding, we again repeat that the Chemists' Building Company is independent of any management from the Chemists' Club. Subscribers to the stock will have a permanent equity in New York real estate, and while their dividends are limited to 3 per cent., so long as the Chemists' Club is in prosperous existence, they are to be shareholders in a well-constructed office building, in the best possible business location, should the Club, for any reason, fail to fulfil its present prospects.

"This is a very different plan from the ordinary scheme, whereby a Club erects its own building on a very slender margin, and obtains additional funds by selling bonds to its own membership, which can only be liquidated through expensive foreclosure proceedings.

"We have, therefore, no hesitation in asking persons who do not themselves expect to profit by the

social advantages of the Club, to subscribe liberally for the erection of the building, which is to be devoted to the advancement of Chemical Science throughout the United States.

"Subscriptions now amount to \$210,000 received from the following subscribers:

"Jerome Alexander, Edward G. Acheson, John Anderson, L. H. Baekeland, Wilder D. Bancroft, John T. Barry, A. A. Breneman, Percy S. Brown, W. Bowman, Chas. A. Browne, E. A. Byrnes, Cassella Color Co., C. F. Chandler, W. B. Cogswell, B. F. Drakenfeld & Co., Dr. J. Douglas, Wm. H. Erhart, Arthur H. Elliott, Fritsche Bros., General Chemical Co., Wm. S. Gray, Grasselli Chem. Co., Theo. Geisenheimer, Edward Gudemán, Mrs. Esther Harrmann, Jacob Hasslacher, Heyden Chemical Works, Dr. C. F. Hirschland, A. von Isakovics, H. J. Krebs, A. Kuttroff, Leger Aniline & Extract Co., Morris Loeb, H. Lieber, A. Lichtenstein, A. R. Ledoux, Adolph Lewisohn, A. C. Langmuir, Parker C. McIlhiney, H. A. Metz, John McKenison, Jr., Dr. McKenna, Wm. H. Nichols, Niagara Electrochem. Co., Nichols Copper Works, Nat'l Aniline & Chem. Co., Emil Pfizer, Chas. Pfizer, Jr., Herbert Philipp, A. L. Plaut, Powers-Weightman-Rosengarten Co., Franz Roessler, Roessler & Hasslacher Chem. Co., Clifford Richardson, W. E. Rowley, I. F. Stone, Nathan Sulzberger, C. C. Speiden, C. F. Stiefel, Schoellkopf, Hartford & Hanna Co., R. Seldner, Henry M. Toch, Maximilian Toch, J. Takamine, C. P. Townsend, A. P. Van Gelder, Dr. Edward Weston, H. W. Wiley, David Wesson, Dr. Whitney, W. Hull Wickham.

It is noticeable that in practically all of the cities the engineers' clubs are better housed than are the chemists', or, indeed, other scientific organizations representing but a single branch. It is true, that at various points academies of science, scientific museums, and similar institutions are equipped with excellent buildings and apparatus, chiefly, however, for museum purposes. Nevertheless, outside of colleges and universities the scientific branches have altogether inadequate meeting-places. This condition will not obtain for any great length of time; the New York chemists have shown the way and set the pace.

With the increase in the number of chemists working in the pure science and in industrial lines, it may be expected that in the near future we shall see buildings erected in all the principal cities to be used as meeting-places for chemical organizations, for club rooms and for laboratories, following to a large extent the plants developed by the New York members of the profession.

#### THE LENGTH OF A TECHNICAL PAPER.

WE Americans are a busy people and as such are in the habit of using and encouraging the use of time-saving devices in our business. Time is money, especially in business hours, and has a distinct value even in the hours of relaxation, when serious matters are to be considered or read.

The short sermon, terse and meaty and right to the point, is the kind the modern church-goer demands, instead of the hour-long variety of our ancestors.

The presidential message that covers a whole newspaper page is read by comparatively few. If it were boiled down to two or three columns, nearly all would read it entire. As it is, for lack of time most people read abstracts of it, or editorial comments.

Even the advertisement must be short and pithy to be read by many.

Only for purposes of entertainment or recreation, as in the case of lecture, novel or play, does the average busy man tolerate with indifference the long-drawn-out or padded feature of the work, and even then it must be extremely clever, witty or entertaining to merit his approval.

Under every-day business or professional conditions, and applying with special force to technical papers, whether for delivery before scientific bodies or for publication in the journals, a good motto to adopt is "make them shot" if the author desires them to be widely appreciated and read.

How often have we sat through conventions, listening politely to long-winded papers that would seem to never end and from very weariness deprived of the mental effort to comprehend. It reminds us of the old Scotch clergyman, who when asked why he made his sermon so long, replied that he didn't have time to make it shorter.

An author should remember that no one is quite so intensely interested in his particular paper as he is himself, and, perhaps, to a diminishing degree a few other kindred souls pursuing the very same line of work. At the same time there are many others who would like to read it if it were really readable. Many a busy reader in glancing through the columns of a journal sees an article on a subject that casually interests him, which, if short, he would read at once. As it is, the mere length deters him and he passes it by for the time, fully meaning to read it in the future, but probably never doing so.



Having gotten together material for a paper, would it not be well in all cases before submitting it for publication to see if it cannot be pruned down and deprived of useless material, crystallizing out the main features and presenting them tersely, and, if possible, in an entertaining form. The ability to write a technical paper in such a manner that to read it is a pleasure is indeed a rare gift, though by no means an impossible one. To make the paper so concise that those interested will want to read it throughout, and not merely glance it through sufficiently to gather the main points or conclusions is a long step forward.

It is, of course, understood that in long or important investigations it is not always possible to avoid papers of considerable length, but too often, even in these cases, much condensation might with advantage be applied before sending them to the editor.

ALBERT E. LEACH.

## ORIGINAL PAPERS.

### ELECTRIC VACUUM FURNACE INSTALLATIONS IN THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.

By W. C. ARSEM.

Received November 15, 1909.

In 1906 I described an electric vacuum furnace<sup>1</sup> at the Ithaca meeting of the American Electrochemical Society. Since that time other types of vacuum furnace have been developed and installed as a part of the equipment for high tem-

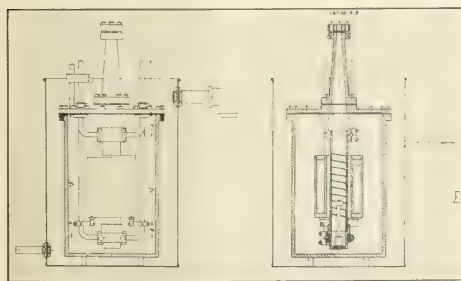


Fig. 1.—Small vertical vacuum furnace.

perature investigations in the General Electric Company's Research Laboratory at Schenectady, N. Y.

The general design of a vacuum furnace comprises a heater enclosed in a vacuum chamber, the heater being of such shape that it almost en-

tirely encloses the object to be heated. The heaters in the various types of furnace differ somewhat, according to the size of the furnace and the use to which it is to be put. In one case the heater is a graphite helix, in an upright position; in another case, it is a horizontal tube; and in another it is composed of 4 grids, made by sawing graphite slabs.

The vacuum chamber is a casting of bronze or gun-metal, the surfaces being machined and tinned to close the pores. All joints are made tight by lead gaskets. The electrode joints have

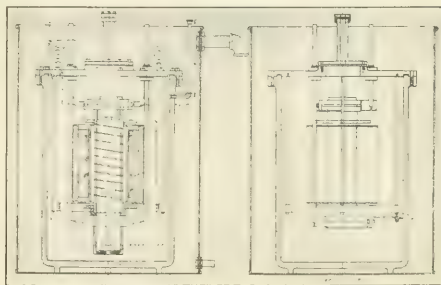


Fig. 2.—Large vertical vacuum furnace.

to be made so that they are air-tight, electrically insulated, and not liable to deterioration by heat. The same type of joint is used on all the furnaces and is illustrated in Fig. 5.

The "radiation screen" is a device for diminishing the amount of heat lost by direct radiation from the heater, and thus increasing the efficiency of the furnace. This is shown by the fact that the temperature *vs.* energy curve is approximately a semi-cubical parabola, whereas without the radiation screen, the curve would follow the Stefan-Boltzmann fourth-power law, like an incandescent lamp.

In the small vertical type furnace, the radiation screen is an annular graphite box, filled with graphite powder which is a poor conductor of heat.

Temperature calibration curves for the vertical furnaces are plotted by means of the equation  $(y-20)^n = ax$ , in which  $y$  is the centigrade temperature of a crucible in the furnace and  $x$  is the corresponding energy in kilowatts. The constants  $n$  and  $a$  are obtained by determining the energy necessary to maintain temperature equilibrium at the melting points of copper and platinum.

In the box type furnace I used Seger cones for calibration, because of their convenience.

Fig. 6 gives examples of calibration curves for the different furnaces.

The laboratory equipment consists of two installations, each containing four vacuum furnaces

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **9**, 153, 171 (1906); *J. Am. Chem. Soc.*, **28**, 921, 935 (1906).



with the necessary transformers, pumps, etc. I shall first describe the different types of furnace:

*Small Vertical Type (Fig. 1).*

This is the type described in the article above referred to. The heater is a vertical graphite helix, in the centre of which may be supported a crucible

using a maximum of 15 kw., but most experiments do not require a higher temperature than 2500° C., which can be attained with 10 kw.

This type of furnace is especially useful for small scale experiments that can be performed in crucibles  $1\frac{1}{2}$ " diameter and 4" high. Of the various

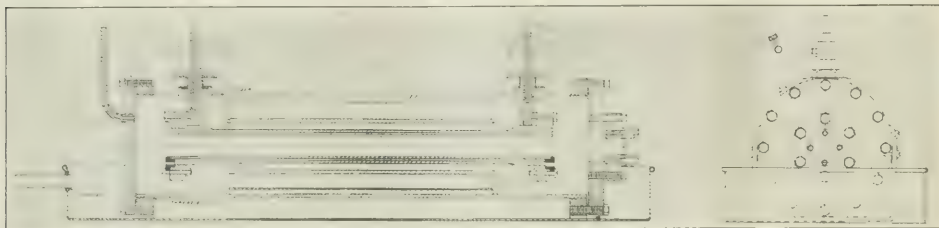


Fig. 3.—Horizontal tube furnace

of carbon, graphite, alumina, tungsten or other material, according to the nature of the experiment.

The temperature can be quickly brought to any desired point, as determined by the calibration curve, and maintained constant for long periods,

uses which naturally suggest themselves, I mention the following:

Preparation of metals, alloys, carbides, silicides and other compounds.

Determination of melting points of metals, alloys, glazes, slags, refractories, etc., by an optical pyrometer, or by reference to the furnace calibration curve.

Calibration of optical pyrometers.

Distillation of refractory substances for separation or purification.

Study of equilibrium in reactions depending upon the pressure of the gaseous phase.<sup>1</sup>

Many reactions can be studied quantitatively with accurately weighed quantities.

*Large Vertical Type (Fig. 2).*

This is similar to the small vertical furnace, but its construction is somewhat modified because of the size and weight of the parts.

The heater is a vertical helix  $5\frac{1}{2}$ " outside diameter,  $4\frac{1}{2}$ " inside diameter, and 21" long. The radiation screen is an annular box, octagonal outside and cylindrical inside, and was built up in sections (see Fig. 11).

A crucible 10" high and 4" in diameter can be heated to 2500° or higher. This is the largest vertical vacuum furnace yet constructed for laboratory use.

It can be used for the same purposes as the

<sup>1</sup> C. A. Hansen, *Electrochem. Ind.*, 7, 427-29 (1909). M. deKay Thompson, *Trans. Am. Electrochem. Soc.*, 1909.

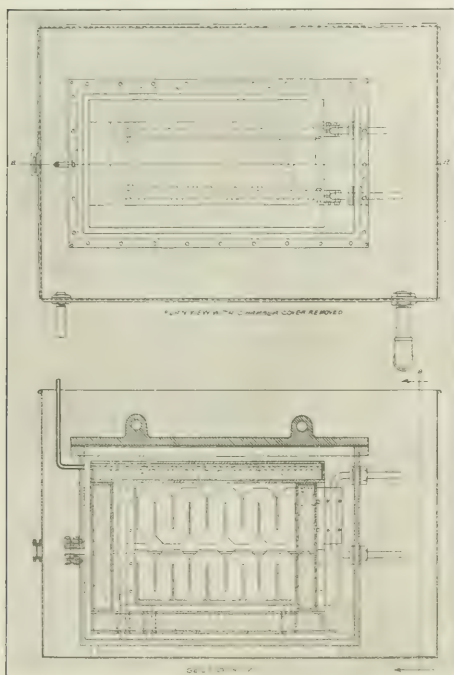


Fig. 4.—Box type vacuum furnace

while the behavior of the article being heated may be observed through the mica window at the top. The range of temperature extends to 3100° C.,

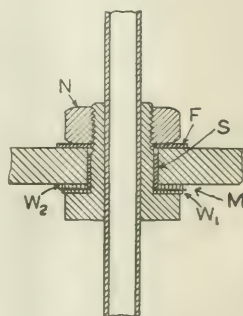


Fig. 5.—Electrode joint: W<sub>1</sub> and W<sub>2</sub>, lead washers; M, mica washer; F, fiber washer; S, fiber sleeve. N, brass nut.

smaller furnace of the same type, with the special advantage of greater capacity. Some of the rarer metals, for instance, can be made in commercially important quantities.

*Horizontal Tube Type (Fig. 3).*

The heater is a thin-walled graphite tube, held in graphite clamps with a tight sliding fit, to permit

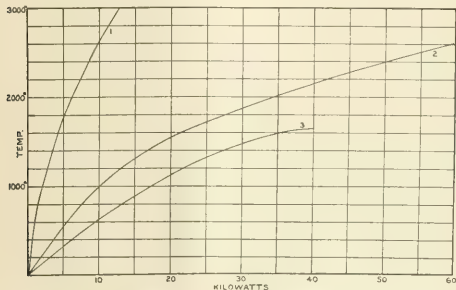


Fig. 6.—Calibration curves. 1, small vertical type; 2, large vertical type; 3, box type.

expansion and contraction. The radiation screen is of the same form as that used in the small vertical furnace, except that its outer wall is made of

brass. The electrode tubes are of somewhat different design from those in the other furnaces, as is seen in the sectional view.

To protect the rather frail heater there is an inner tube of graphite, insulated from the heater at the ends. This inner tube has an internal diameter of  $1\frac{1}{8}$ " and a length of 21", of which 10" is quite uniformly heated. There is a window at one end, for observation purposes.

The furnace is especially well adapted to the annealing or heat treatment of metal bars or rods.

It takes 4 kw. at  $1700^{\circ}$ , or about 400 amperes at 10 volts.

*Box Type (Figs. 4 and 7).*

The chamber of this furnace is a rectangular gun-metal box, with a removable cover. The heater is made up of four graphite grids, connected in series. These grids are made by sawing slots in graphite slabs  $5" \times 18" \times \frac{3}{4}"$ .

The heated space enclosed by the grids is large enough to take a box-shaped crucible 4" wide, 12" long and 8" high, or 384 cubic inches.

The radiation screen is made up of 8 box-like sections, each hollow and fitted with graphite

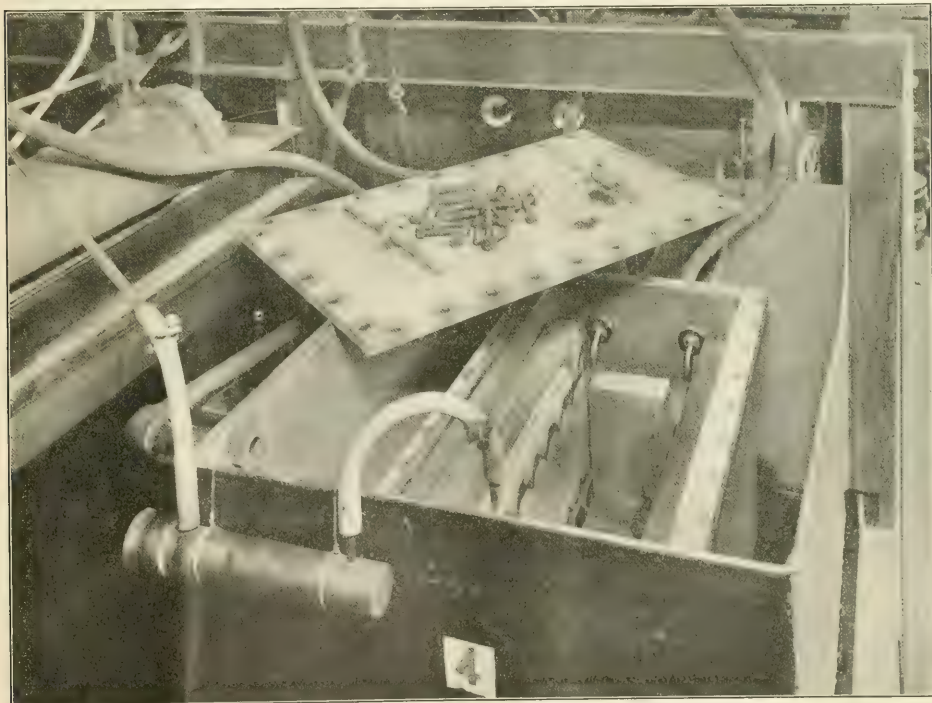


Fig 7 — Box type vacuum furnace.

powder, the top section being removable when charging the furnace.

There is a window at one end of the furnace which is in line with a window in the water-jacket and with a hole in the end section of the radiation screen, thus giving a good view into the hot space. Fig. 7 shows the interior of the furnace, looking from above, the top section of the screen having been removed. The heater grids are plainly visible.

This furnace may be used for making fairly large amounts of materials which are otherwise

1700° C., while that of the large vertical furnace is over 2500° C.

TABLE OF FURNACE DATA.

	Small vertical.	Large vertical.	Horizontal tube.	Box type.
Maximum kilowatts.....	15	60	4	40
Maximum current, amperes.	250	800	400	570
Maximum voltage.....	60	75	10	70
Maximum temperature.....	3100°	2600°	1700°	1700°
Crucible volume.....	5 cu. in.	125 cu. in.	7.8 cu. in.	344 cu. in.
Crucible height.....	4 in.	10 in.	10 in.	8 in.
Crucible section.....	1 1/4" diam.	4" diam.	1" diam.	4" by 12"
Height of furnace.....	21 in.	48 in.	15 in.	24 in.
Base of furnace.....	15" diam.	36" diam.	12" by 36"	24" by 36"

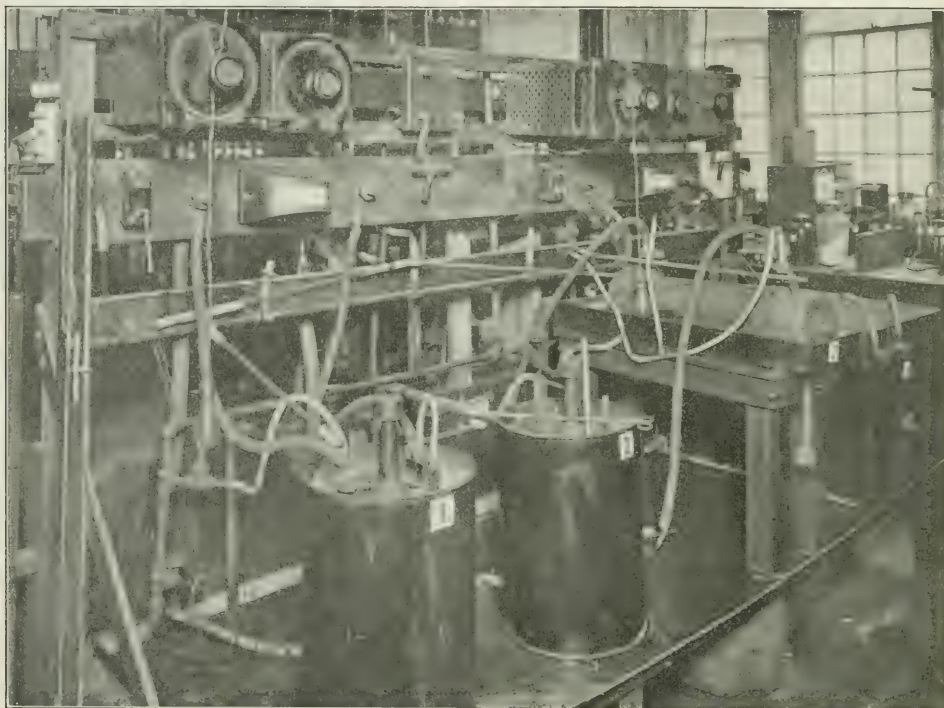


Fig. 8 —Front of Installation A.

difficult to produce, as, for example, certain rare metals which can be made in quantities of several pounds by reducing their oxides by carbon.

To perform such an experiment it is the work of only a few moments to put the charge in, fasten the cover down, exhaust the furnace, and start the run. As the temperature of the reaction is under perfect control and the material not exposed to oxidizing influences, the conditions are ideal.

The capacity of this furnace is considerably greater than that of the large vertical type, but its temperature limit in its present form is about

#### Installation A.

This installation consists of four furnaces. No. 1 and No. 2 are of the small vertical type, No. 3 horizontal tube type, No. 4 of the box type. These furnaces are set up in a row upon a low bench, having a galvanized iron top made in the form of a shallow pan, which drains into a deep sink behind the furnaces. This arrangement takes care of the outflow from the water jackets of the furnaces. Behind the furnaces are arranged the pump and the transformers.

Furnaces Nos. 1 and 2 are operated by a 25 kw.



transformer, and Nos. 3 and 4 are run on a "flux shunt" transformer, such as is used for thawing water-pipes. This is rated at 30 kw., but can be overloaded to 40 kw. for short periods. The energy supply to the furnace is usually controlled by rheostats in the field circuit of the generator supplying the current. The "flux-shunt" transformer, however, may be connected to any 1100 or 2200 volt circuit, and the voltage on the secondary side, which is connected to the furnace, may be regulated by simply turning a hand-wheel to raise or lower the "flux-shunt."

0.03 mm. of mercury in a cold furnace of the small vertical type.

The pressure during a run depends, of course, upon the nature of the charge, but an excellent vacuum can be maintained at the highest temperatures if the charge does not liberate gases.

Between the furnaces and transformers stands a switchboard upon which are mounted the switches, field rheostats, wattmeters, and transformer terminals. Water for cooling purposes is supplied by a tap near each furnace.

At the end of the switchboard stands a McLeod

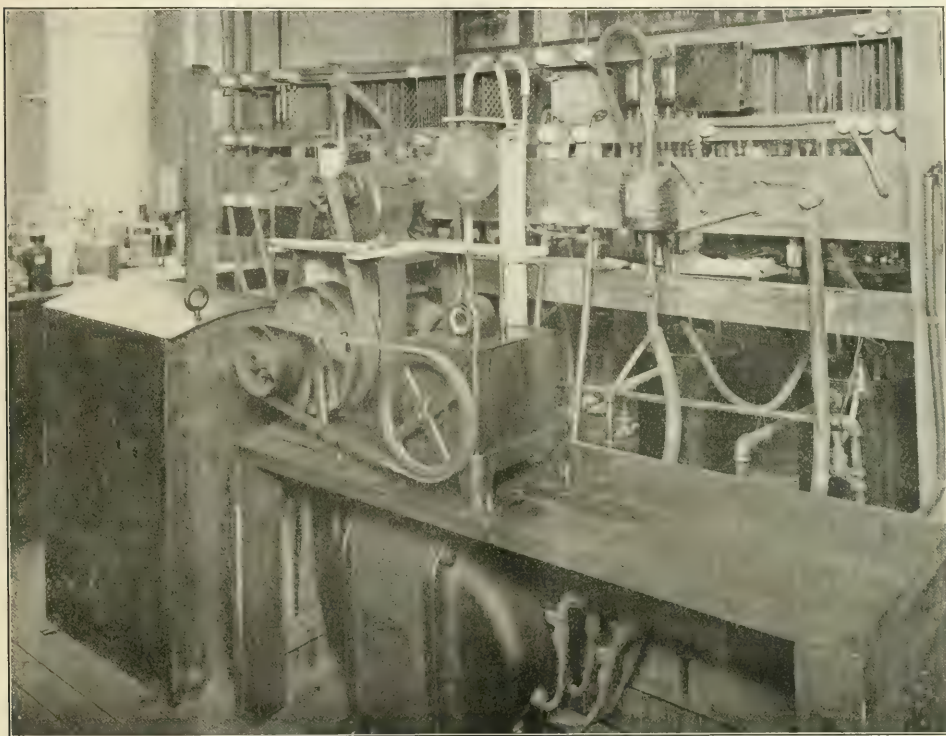


Fig. 9.—Back of Installation A.

The Siemens-Schuckert rotary oil-pump used for evacuating the furnaces is mounted on a bench over the 25 kw. transformer, the discharge side of the oil-pump being connected to the laboratory "rough-pump." In exhausting a furnace it is customary to first reduce the pressure to 4 or 5 mm. by means of the rough pump, and then to use the rotary pump to get a vacuum good enough for operating the furnace. With the rotary pump there is no difficulty in reducing the pressure to

gauge for measuring pressure in the furnaces more accurately than can be done with an ordinary manometer.

Figs. 8 and 9 show the front and back of installation A.

#### *Installation B.*

This installation consists also of four furnaces. Nos. 5 and 6 are small vertical furnaces, No. 7 is a box type, and No. 8 is a large vertical furnace.

Two double-cylinder Geryck pumps and a three-

cylinder Packard pump are used for evacuation, in connection with the laboratory "rough pump."

Regular General Electric Type H transformers are used to supply current, regulation being effected by field control. The usual form of mercury manometer is used here.

These furnaces are in charge of a skilled furnace operator, who performs any experiments desired by the members of the laboratory force.

A general view of this installation is shown in Fig. 10.

The heaters are inexpensive, and the replacement of one is a very simple matter.

Over 500 runs have been made in one of the small vertical furnaces, and over 200 runs in the box-type furnace No. 4. The total number of runs made in all these furnaces to date is about 2000.

A number of institutions of learning have installed small vertical vacuum furnaces in their electrochemical departments. Among these are Cornell, Mass. Institute of Technology, New Hampshire College and Rensselaer Polytech. Inst. The

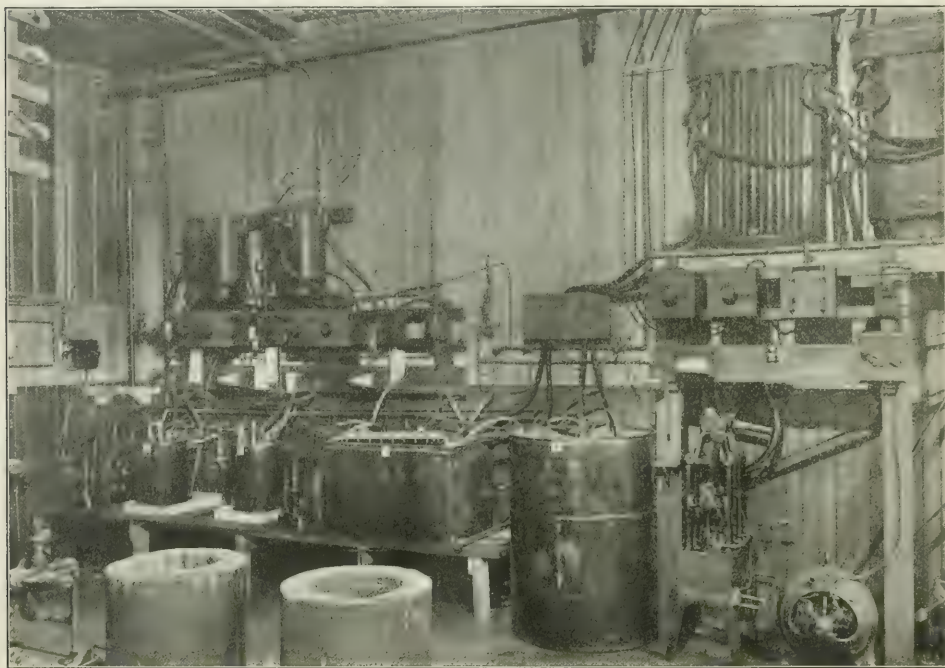


Fig. 10.—Installation B.

As regards the durability of these furnaces, the following may be of interest.

Since the furnaces are evacuated, there is, of course, no wasting of the heater and other graphite parts by oxidation.

Volatilization or disintegration of graphite begins to be apparent at  $2500^{\circ}\text{C.}$ , so that at this temperature a heater will waste away at its middle point in about 9 hours, while at  $3100^{\circ}$  it will last less than one hour. Up to  $2000^{\circ}$ , however, graphite does not volatilize appreciably, so that a heater which is never run above this temperature ought to last indefinitely.

Bureau of Standards at Washington also has a furnace.

In designing installations where field control as a means of regulating the voltage on the furnace is not permissible, several other means of securing variable voltage are available:

1. A transformer with a series of taps giving different voltages.
2. An ordinary transformer used in connection with an induction regulator.
3. A "flux-shunt," or pipe-thawing transformer.

A very convenient installation for small scale experimental work would consist of a small vertical



type<sup>1</sup> vacuum furnace, a 10 kw. "flux-shunt transformer, a Geryck pump, and a 15 kw. wattmeter.

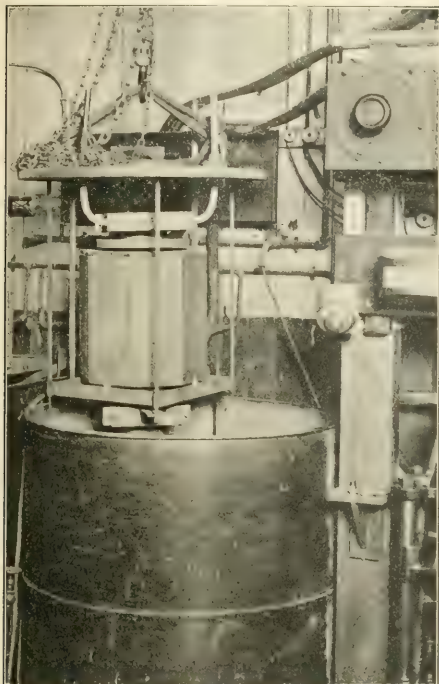
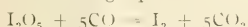


Fig. 11.—Large vertical type vacuum furnace, showing radiation screen.

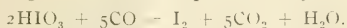
## THE DETERMINATION OF CARBONIC OXIDE IN ILLUMINATING GAS BY IODINE PENTOXIDE.

By AUGUSTUS H. GILL AND EDWARD H. BARTLETT.

The reaction made use of in this method for the quantitative determination of carbon monoxide is that first indicated by Ditte.<sup>1</sup> He showed in 1870, that if carbon monoxide was passed over iodine pentoxide at temperatures between 150° and 200° C., a reaction ensued by means of which the carbon monoxide was oxidized to carbon dioxide, this action being accompanied by a simultaneous reduction of the  $I_2O_5$  to free iodine, expressed by the following equation:



An analogous reaction is produced by iodic acid,



Apparently the first to actually make use of this reaction were de la Harpe and Reverdin,<sup>2</sup> who used it in 1888 for the detection of carbon

monoxide in the atmosphere. They passed filtered air over dry iodic acid heated to 150° C. and then into a solution of starch paste. If the air contained carbon monoxide this fact was made apparent of the blue color in the starch solution.

Phillips,<sup>1</sup> in 1894, mentions this reaction, and says that before it can be used for analytical work it is necessary to remove the higher olefines, acetylene, and vapors of benzene and alcohol. He says further that the lower paraffins are without action on the iodine pentoxide up to temperatures at which the iodic acid dissociates.

In 1898 both Nicloux and Gautier report having used this reaction quantitatively. Gautier did not publish his method until after that of Nicloux had appeared. He claims, however, to have been using his method for several years previously. Both confined their attention to the determination of carbonic oxide in the small quantities in which it is met with in the air.

Nicloux<sup>2</sup> first removed carbon dioxide, sulphuretted hydrogen, sulphurous acid and water vapor from the air, and passed it over iodic anhydride at a temperature of 150°. The iodine set free was carried along by the stream of air through a tube filled with a solution of potassium hydrate—where it was absorbed. The amount of iodine was then determined by the method of Rabourdin, which consists in acidifying the potassium hydrate solution with sulphuric acid, adding a few centigrams of nitrite of soda and 5 cc. of chloroform or carbon bisulphide, and then shaking the whole vigorously. This sets free the iodine which is then taken up by the chloroform or carbon bisulphide; the color of the solution obtained is compared with the color produced from a solution of potassium iodide, the strength of which is determined by titration. Nicloux tested this method by using air, the contents of which in carbonic oxide varied from 1 part in 1000 to 1 part in 50,000. He reports his results to have shown the method to be very accurate. He also says that neither hydrogen nor methane give an analogous reaction at this temperature.

Gautier<sup>3</sup> devised two quantitative methods using this reaction. In his first method, he passed the air first through a tube containing  $I_2O_5$ , and then through a small tube filled with pulverulent copper. The iodine set free by the reaction was taken up from the air by copper, after which its weight was obtained by taking the difference between the weights of the tube of copper before and after the experiment. Gautier soon abandoned this method, however, for another one in which he determined

<sup>1</sup> *Am. Chem. Jour.*, **16** (1894).

<sup>2</sup> *Compt. rend.*, **126**, 746.

<sup>3</sup> *Ibid.*, **126**, 793 and 931.

<sup>1</sup> *Bull. Soc. Chim.*, **13**, 318.

<sup>2</sup> *Chem. Z.*, **12**, 1726.

the amount of carbon dioxide formed instead of the iodine set free. He now passed the air after it had been in contact with the iodine pentoxide into a tube filled with glass beads, which contained a known volume of potassium hydrate solution free from carbonate. The carbon dioxide thus absorbed was again reobtained in the gaseous state by neutralizing the potassium hydrate solution with sulphuric acid. The volume of carbon dioxide thus obtained equaled the volume of carbonic oxide in the volume of air taken for analysis. Gautier investigated the accuracy of this method, using dilutions of carbonic oxide varying from 1 part in 500 to 1 part in 30,000 and keeping the tube of iodine pentoxide at temperatures ranging from 65° to 80°. He states that the method is fully accurate enough for practical purposes.

Gautier says that he has observed that the oxidation of the carbonic oxide begins at temperatures of less than 30° C., that it is active between 40° and 45°, and complete at 60°–65°. He says that this is true whatever be the dilution of the carbonic oxide in the air. With the exception of acetylene he says further that most of the hydrocarbons are not acted upon by iodine pentoxide at these temperatures. Certain gases like ethylene, however, although themselves being oxidized very difficultly at these temperatures, nevertheless have the property of hindering greatly the oxidation of carbonic oxide. He says further that contrary to the general rule this reaction goes completely, the carbonic oxide being oxidized to the very last trace. For every cubic centimeter of carbonic oxide at 0° and 760 mm. there is set free 0.00227 gram of iodine. Finally, he says that at these temperatures, 65°–80°, methane and hydrogen are not oxidized.

The problem of adopting this reaction for use in the determination of the carbonic oxide in the atmosphere was next taken up by Kinnicutt and Sanford<sup>1</sup> in 1899. By way of premise they say that all the methods which have been used for this purpose may be divided into two classes, to wit: those employing the reaction between carbon monoxide and the haemoglobin of blood by means of which carbon monoxid haemoglobin is formed, and those in which carbonic oxide is oxidized to carbon dioxide. The processes of the first class are of but little value from a quantitative standpoint. The most suitable oxidizing agent for use in the processes of the second class has been found to be iodine pentoxide. They report that they experimented with the methods of Nicloux and Gautier, and failed in both instances to obtain accurate results. They then proceeded to devise a method of their own. Their method is a modi-

fication of that of Nicloux. They passed the air first through a tube containing pieces of stick potash and a tube containing sulphuric acid, in order to remove from it sulphuretted hydrogen, sulphurous acid and similar reducing gases and all unsaturated hydrocarbons. They then passed the air through a tube containing iodine pentoxide heated to a temperature of 150°, after which it was passed into a solution of potassium iodide which absorbed the iodine. Finally they titrated this solution with a N/1000 sodium thiosulphite solution to determine the iodine. By measuring the carbonic oxide used in making up their samples in capillary tubes, they were enabled to read the volume to 0.001 cc. The content of carbonic oxide varied from 1 part in 2440 parts of air to 1 part in 43,479 parts of air. They report the results of fourteen analyses which show the method to have been very accurate. They found that they could determine as little as 2.5 vols. of CO in 100,000 volumes of air.

They next made experiments to determine whether or not the presence of illuminating gas in the air would vitiate the accuracy of these results. They found that the presence of the gas had no disturbing effect whatever, as is shown by the following results:

	cc.	cc.
Carbonic oxide calculated.....	0.0191	0.02789
Carbonic oxide found.....	0.019	0.027

This indicated that hydrogen and methane were not acted upon at this temperature. They had previously made experiments which had shown the same result. They also made experiments which showed that the reaction was not quantitative at temperatures lower than 150°. This is in direct contradiction to Gautier who says that the reaction is complete at temperatures as low as 60°–65°. These results of Kinnicutt and Sanford show that this method gives very accurate results when applied to the determination of carbonic oxide in the small quantities which are found in the atmosphere.

In 1900 Smits, Raken, and Terwogt,<sup>1</sup> of the University of Amsterdam, proposed utilizing this oxidation of carbon monoxide for its quantitative determination in the analysis of illuminating gas. After reviewing briefly the work of Nicloux and Gautier, they say that it is obvious that this "very sensitive" reaction, heretofore only used in the analysis of air, is also applicable to the determination of carbon monoxide in illuminating gas. They say, however, that it is out of the question to think of placing the carbonic oxide determination in line in a complete gas analysis, if the exact method of either Nicloux or Gautier is used. They

<sup>1</sup> Jour. Am. Chem. Soc., 22, 14.

<sup>1</sup> Zeit. für angew. Chem., 1900, 1002.

therefore modified Gautier's method and proceeded as follows: The gas from which the carbon dioxide, the illuminants, and oxygen had been removed in the ordinary Hempel scheme of analysis, was passed from a Hempel burette, through a U-tube containing iodine pentoxide heated to 150° by an oil bath into a Hempel pipette containing a solution of caustic potash. The caustic potash absorbed the carbon dioxide formed by the oxidation of the carbonic oxide so that the contraction in volume after the absorption was complete gave the volume of the latter present. The correction for the vapor tension of iodine was found to be negligible. It does not appear from their article that they ever actually tried their method in an actual analysis of illuminating gas. They did, however, undertake to find out whether or not hydrogen or methane would undergo oxidation on being passed through the iodine pentoxide tube. To this end they made by their method an analysis of a mixture of hydrogen and carbon monoxide, and another analysis of a mixture of methane and carbonic oxide. They report the following results:

	Found, cc	Mixed, cc
Hydrogen.....	72.7	72.6
Carbon oxide.....	8.7	8.8
Methane.....	42.7	42.8
Carbon oxide.....	8.1	8.0

It will be noticed that they give results for two experiments only, and that neither of these properly represents the conditions of practice, as in neither were both hydrogen and methane associated with the carbon monoxide. They do not hesitate, however, to say that their method is very exact and much superior to that in ordinary use.

The method of determination of carbonic oxide by cuprous chloride is so unsatisfactory that it was thought this promised well, and their work was repeated with the following results:

TABLE I.—SHOWING ABSORPTION OF CARBONIC OXIDE BY IODINE PENTOXIDE.

CO used.	CO found.	Loss.	Per cent. lost.	Bath temp.	Time, min.
21.8	20.8	1.0	3.6	150	90
23.2	22.2	1.0	4.3	150	150
25.9	25.5	0.4	1.0	152	32
25.6	25.6	0.0	0.0	154	29
26.4	26.0	0.4	1.0	161	32

In the last three results the carbonic oxide was mixed with air. It will be noticed that after two and a half hours' passage of the gas through the tube more than 4 per cent. of the gas remained unabsorbed. This would seem to show the impracticability of the method.

To still further test the method a mixture of carbonic oxide, methane, hydrogen and nitrogen was made of about the composition of that left after carbon dioxide, "illuminants" and oxygen had been absorbed from an illuminating gas and

passed through the iodine pentoxide. The results are shown in Table II.

TABLE II.—ABSORPTION OF CARBONIC OXIDE BY IODINE PENTOXIDE FROM MIXTURE OF GASES.

Hydrogen.	Meth- ane.	Carb. oxide added.	Carb. oxide found.	Gain.	Per cent. gain.	Bath temp.	Time, min.
24.1	44.8	25.6	28.5	2.9	11.3	157	24
24.4	42.3	26.4	31.3	4.9	18.6	152	29
23.6	46.1	25.6	27.1	1.5	5.9	152	28
26.1	46.2	24.1	27.1	3.0	12.4	152	51
24.6	53.5	25.7	28.1	2.4	9.3	152	75
20.4	43.7	27.8	31.5	3.7	13.3	148	30
24.0	46.0	26.1	26.9	0.8	3.1	150	26

It will be noticed from this table that the amount of carbonic oxide found considerably exceeds the amount originally added: The errors of the analysis are not sufficient to account for this and they show no regularity. Moreover, another observer a year previously had obtained almost identical results, the average error found by him being 7.8 per cent., whereas the average error of these results is 9.1. This error, as was shown by two different observers working independently, is not due to the action of the iodine pentoxide upon either the methane or the hydrogen nor the number of times the tube had been used nor the length of time taken by the gas in passing through the tube, but may be due to the breaking up of the iodine pentoxide.

In conclusion it may be said that the method of absorption of considerable quantities of carbonic oxide by iodine pentoxide is inaccurate, irregular in action and tedious and troublesome to use.

Finally our acknowledgments are due to Messrs. J. B. Finnegan and R. W. Lindsay by whom some of the experiments here detailed were performed.

## THE COEFFICIENT OF EXPANSION OF GLYCERINE.

By ARTHUR M. COMBIE AND CECIL F. BACKUS.

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Upon examination of the literature on the coefficient of expansion of glycerine, it was found there was some discrepancy between various authorities. Hehner<sup>1</sup> states that it amounts to 0.00058 for each degree centigrade in the neighborhood of 15.5° C. It can be calculated from the results of Gerlach's observations<sup>2</sup> that the value of this factor varies with the temperature according to the following table:

Tempera- ture.	Coefficient of expansion.
5.0°	0.00057
12.5°	0.000587
20.0°	0.00060
30.0°	0.000619

The necessity of using an accurate coefficient in figuring the results obtained by determining

<sup>1</sup> J. S. C. I., 8, 8 (1889).

<sup>2</sup> Zeit. anal. Chem., 24, 111.



the specific gravity of glycerine at temperatures varying considerably from 15.5° led to the following investigation:

*Weights and Balances Used.*—The weights and balances used in the following determinations were carefully checked just before beginning the work. The weights that showed slight errors were adjusted so that each was a multiple of the other. The balance beam was found to give accurate weighings when the load and weights were shifted to opposite pans.

*Water Bath.*—The water, or constant temperature bath, employed to keep the pycnometers at 15.5°, 20°, 25° and 30° C. for the standardizations and determinations consists of two wooden boxes with an air space of one inch between the sides and bottom. The inner box is twenty inches long, fifteen inches deep and fifteen inches wide, lined with tin, having a shelf 10 × 8 inches, eight inches from the bottom. The bath was filled with water so that it covered the shelf to a depth of four and one-half inches. When the pycnometers are set upon the shelf with the water at this depth, the capillaries are entirely submerged, the rubber tubing, described later, serving to protect the contents of the pycnometer. By entirely submerging the body and capillary of the pycnometers, the contents are brought to the same temperature throughout. After the proper temperature was attained, the water was bailed out or drawn off until about one-half inch of the capillary projected out of the water. The temperature of the bath can be regulated by the addition of small pieces of ice, cold water, or hot water to within very narrow limits—less than 0.05° C.

Several small streams of air served to keep the water agitated, the temperature of the bath being the same at all points at a given time.

*Pycnometer.*—Geissler specific gravity bottles of 50 cc. capacity with centigrade thermometer graduated to 0.2° ground into neck of bottle, and with side capillary tube with ground glass cap were used in these determinations.

*Detailed Description of the Method Employed for the Standardization of Pycnometers.*—Freshly boiled, distilled water was rapidly cooled to about 15° C. in a flask which was covered with a watch-glass to keep out the air. The capillary of the pycnometer was inserted into a piece of clean and dry rubber tubing (2.5 mm. in diameter), which was fitted snugly over the capillary and which was 63 mm. in length. The pycnometer was then carefully filled with the air-free, distilled water by pouring down the side and the thermometer set firmly in place. It was then placed in the water bath and after the pycnometer-thermometer and the standard thermometer reached 15.5° C.,

the temperature was kept constant for fifteen minutes more.

The pycnometers were submerged about four and one-half inches in the water bath during the time required for the water in them to attain the desired temperature. The water in the bath was then drawn off until about one-half inch of the capillary projected out of it. The rubber tubing was then removed and the top of the capillary wiped with a dry finger before removing from the water bath. The pycnometer was taken from the bath immediately after the excess water was removed from the top of the capillary and the ground portion of the capillary wiped with a piece of filter paper and the cap placed on tight. The whole pycnometer was then quickly dried by wiping with a dry cloth and weighed as rapidly as possible, without swinging the balance (which is sensitive to 0.2 mg. without swinging) to the fourth decimal place. The pycnometers were all standardized at the same time, but each one was weighed before the next was taken out of the water bath, due to the fact that there is a gradual loss of weight if the pycnometers stand for even a few minutes when they contain water. The loss of water is probably due to evaporation through the ground glass joint between the pycnometer and the thermometer.

The water that is forced through the capillary into the rubber tube when the thermometer is set in place is enough to replace any contraction due to lowering of the temperature, provided the difference in temperature is not too great. The rubber tube also allows the capillary to be entirely immersed and yet keeps out the water of the bath.

*Standardization of Pycnometer-Thermometers and Pycnometers.*—The pycnometer-thermometers were compared with a standard thermometer, which has been checked against several good thermometers at four points, *viz.*: 15.5°, 20°, 25° and 30°, and corrections were applied whenever needed.

The capacities of the pycnometers were determined in duplicate in a water bath at 15.5° C., while the temperature of the room registered 18° to 20° C. The capacities at 15.5° C. for two of the pycnometers checked results obtained some time previous at room temperatures and figured to grams of water at 15.5° C. From the weight of water obtained at *t* degrees the capacity at 15.5° is obtained from the following formula:

$$C = W \frac{D}{d} \frac{1}{1 + a(t - 15.5)}$$

in which,

*t* = Observed temperature.

*W* = Capacity in grams of water at *t*° C.

*D* = Density of water at 15.5° C.

*d* = Density of water at *t*° C.

$a$  = Coefficient of cubic expansion of glass, which is taken as 0.000025 per  $1^{\circ}\text{C}$ . between  $15.5^{\circ}$  and  $30^{\circ}\text{C}$ .

$C$  = Capacity in grams of water at  $15.5^{\circ}\text{C}$ .

Table I gives the capacities found and the corrections applied to the thermometers.

TABLE I.—CAPACITIES AND THERMOMETER CORRECTIONS FOR PYCNOMETERS.

Pycnometer marked.	Duplicate determinations at $15.5^{\circ}$ .	Average capacity used at $15.5^{\circ}$ .	Average determinations at $t^{\circ}\text{C}$ .	Thermometer corrections.			
				$15.5^{\circ}$ .	$20.0^{\circ}$ .	$25.0^{\circ}$ .	$30.0^{\circ}$ .
A.....	{ 49.7422 49.7422	49.7422	49.7421	0	0	0	-0.20
B.....	{ 50.2178 50.2182	50.2180	50.2179	0	0	0	0
C.....	{ 50.1063 50.1063	50.1063	.....	-0.10	-0.20	-0.20	-0.30
G.....	{ 49.6595 49.6596	49.6596	.....	-0.10	-0.05	-0.10	-0.10
H.....	{ 49.9742 49.9736	49.9739	.....	-0.10	-0.10	-0.10	-0.15
I.....	{ 49.9535 49.9537	49.9536	.....	-0.05	-0.10	-0.20	-0.25
J.....	{ 50.7740 50.7743	50.7742	.....	-0.10	0.15	-0.20	-0.15
K.....	{ 50.2140 50.2140	50.2140	.....	0	0	-0.10	-0.10
L.....	{ 50.1220 50.1217	50.1219	.....	0	0	-0.10	-0.15
M.....	{ 50.0172 50.0168	50.0170	.....	-0.10	0	-0.05	-0.05
N.....	{ 49.5540 49.5541	49.5541	.....	0	0	+0.05	0

*Detailed Description of the Specific Gravity Determinations; Glycerine Used and Method of Transferring it from the Large Sample Bottles to the Pycnometers.*—Several samples of dynamite glycerine were used in these determinations, which had been obtained from different manufacturers. These were tested as received and also diluted to cover specific gravities ranging from 1.254 to 1.264. The glycerine sample in each case was thoroughly shaken at times on three successive days and then allowed to stand four days to free itself of air bubbles before making the determinations. The glycerine was transferred directly from the centre of the large sample bottles to the pycnometers, through a siphon arrangement. With a slight air pressure, the glycerine would flow as rapidly as desired without air bubbles, thus eliminating the danger of any diluted glycerine from the neck of the sample bottle or from the surface of the sample getting into the pycnometer.

*Specific Gravity Determinations.*—The pycnometer was first dried with alcohol and ether and then subjected to a current of dry air to remove all traces of ether, weighed and filled by allowing the glycerine to flow from the bottle through the siphon arrangement down the side as rapidly as possible. When filled, the thermometer was inserted into the neck of the pycnometer until the glycerine stood in a globule on top of the capillary. A small quantity of glycerine was then drawn from the large sample into a small, dry beaker

and a dry rubber tube 2.5 mm. in diameter and 63 mm. in length, supplied with a glass tube drawn out to a fine capillary, was then filled from it by drawing up some of the glycerine. The rubber tube full of glycerine was then quickly placed on the capillary of the pycnometer and the thermometer set firmly in place. This forced the excess of the glycerine through the capillary into the rubber tube and out through the small capillary. A neater way of manipulating the rubber tube attachment would be to first put it on the pycnometer, fill the pycnometer with glycerine to overflowing and then draw the tube full of glycerine before inserting the thermometer. The pycnometer was then submerged to a depth of  $4\frac{1}{2}$  inches in the water bath, which was kept first at  $15.5^{\circ}$ , then at  $20^{\circ}$ ,  $25^{\circ}$  and  $30^{\circ}\text{C}$ ., and allowed to remain for ten or fifteen minutes longer after its thermometer and the standard thermometer in the bath registered the desired temperature. The extra time allowed for the glycerine in the pycnometer to attain a uniform temperature throughout may not have been necessary but was allowed as a precaution.

Just before the pycnometer was ready to be taken from the bath, the water was drawn off until its capillary projected about one-half inch above the water. The rubber tube was then carefully removed, the excess glycerine wiped from the top of the capillary with a dry finger, the pycnometer quickly removed from the bath and the ground portion of its capillary wiped dry with a piece of filter paper and the cap placed on tight. The pycnometer was then wiped first with a wet and then with a dry cloth until dry and allowed to stand until it had attained the temperature of the room before weighing. Moisture collects very rapidly in damp weather upon the surface of the pycnometer when its temperature is below room temperature. There is no loss in weight upon standing when the pycnometer contains glycerine, as is the case when it contains water, for glycerine is more viscous and less volatile than water. The specific gravity was first determined at  $15.5^{\circ}\text{C}$ . and successively at  $20^{\circ}$ ,  $25^{\circ}$ , and  $30^{\circ}\text{C}$ ., using the same pycnometer containing the same glycerine for all four determinations, for as the temperature increased the glycerine expanded and was forced out into the rubber tube, which was filled with glycerine each time as described above.

The rubber tube attachment permits the glycerine to be transferred from the sample bottle at room temperature to the pycnometer without first changing its temperature if the specific gravity is to be determined in the water bath at any temperature between  $15.5^{\circ}$  and  $30^{\circ}\text{C}$ . A tube of the size mentioned above with a glass capillary



will hold enough glycerine to supply the deficiency caused by contraction due to a reduction in temperature of 20° C. with a liberal excess. It also allows the pycnometer to be submerged to a depth of four and one-half to five inches in the bath whereby all of its contents attain the same temperature throughout, while the capillary admits air and keeps out the water. Even though water were to get into the rubber tube, the viscosity of the glycerine would not allow it to get into the pycnometer. This was proven by three of the pycnometers being overturned in the water just after

C = Capacity of pycnometer in grams of water at 15.5°.

a = Thermal coefficient of expansion of glass = 0.000025 per 1° C.

B = Thermal coefficient of expansion of glycerine.

t = Observed temperature.

*Explanation of Tables:*

Table I shows the pycnometers used, their capacities and thermometer corrections.

Table II shows the glycerine used, the specific gravity determinations made at 15.5° C., with the

TABLE II.—SPECIFIC GRAVITY AT 15.5° AND AT 20°, 25° AND 30° C.  
CALCULATED FROM THE FORMULA  $\frac{W}{C} \frac{1}{1 + a(t - 15.5)}$  WITHOUT CORRECTION FOR EXPANSION OF GLYCERINE.

Glycerine. (1).	Sp. Gr. at 15.5° (2).	Av. sp. gr. at 15.5° (3).	Specific gravity at 20° without glycerin expansion correction.		Specific gravity at 25° without glycerin expansion correction.		Specific gravity at 30° without glycerin expansion correction.		Pyc- nometer used. (10).
			Results. (4).	Average. (5).	Results. (6).	Average. (7).	Results. (8).	Average. (9).	
A.....	1 25465	1 25465	1.25190	1.25190	1.24878	1.24878	1.24564	1.24564	A
	1 25465		1.25190		1.24877		1.24564		C
	1 25736		1.25461		1.25149		1.24836		G
B.....	1 25736	1 25736	1.25461	1.25461	1.25148	1.25149	1.24833	1.24835	H
	1 26010		1.25735		1.25422		1.25108		I
C.....	1 26013	1 26012	1.25737	1.25736	1.25423	1 25423	1.25108	1.25108	J
	1 26023		1.25746		1.25435		1.25123		M
D.....	1 26029	1 26026	1.25751	1.25749	1.25440	1 25438	1.25129	1.25126	N
	1 26078		1.25801		1.25492		1.25177		A
E.....	1 26075	1 26077	1.25798	1 25800	1.25489	1 25491	1.25174	1.25176	C
	1 26135		1.25858		1.25548		1.25233		G
F.....	1 26135	1.26135	1.25858	1 25858	1.25547	1.25548	1.25232	1.25233	H
	1 26175		1.25897		1.25587		1.25272		I
G.....	1 26178	1.26177	1.25901	1 25899	1.25591	1.25589	1.25273	1.25273	J
	1 26239								G
	1 26240								H
H.....	1 26232	1 26238		1 25965		1 25659		1 25348	I
	1 26238		1.25965		1.25659		1.25346		K
	1 26241		1.25965		1.25659		1.25348		J
	1 26238		1.25965		1.25659		1.25349		M
	1 26314		1.26037						H
I.....	1 26313	1.26312	1.26037	1 26037	1.25725	1.25728	1.25414	1.25416	I
	1 26309		1.26037		1.25730		1.25417		H
	1 26339		1.26064						A
	1 26342		1.26066						C
	1 26347		1.26072						G
J.....	1 26336	1.26340	1.26065	1 26067	1.25758	1.25759	1.25446	1.25448	A
	1 26338		1.26066		1.25758		1.25447		C
	1 26341		1.26072		1.25761		1.25451		G
	1 26365		1.26087		1.25780	1.25783	1.25466	1.25469	M
	1 26370		1.26094		1.25786		1.25472		N
K.....	1 26417	1.26368	1.26138	1.26092		1.25783		1.25466	J
	1 26414		1.26136						M
	1 26420		1.26142						N
	1 26419		1.26136		1.25827		1.25513		J
	1 26417		1.26135		1.25828	1.25829	1.25513	1.25515	M
	1 26421		1.26139		1.25833		1.25518		N

being put into the bath, the determinations being completed and afterward redetermined to make sure that they were correct.

*Formula for Calculating the Specific Gravity of Glycerine at 15.5° C. when Determined at t Degrees Centigrade.*—

Specific Gravity at

$$\frac{15.5^\circ}{15.5^\circ} = \frac{W}{C} \frac{1}{1 + a(t - 15.5)} + B(t - 15.5)$$

in which

W = Weight of glycerine at t°.

average, the specific gravity without the coefficient of expansion correction at 20°, 25° and 30° C., with the averages and the pycnometer used in each determination.

Table III:

Column 1.—Glycerine used.

Column 2.—Specific gravity at 15.5° C.; Table II, column 5.

Column 3.—Specific gravity at 20° C. without glycerine expansion correction; Table II, column 5.

Column 4.—Difference between specific gravity

at 15.5° and 20° C. without glycerine expansion correction.

Column 5.—Expansion correction per degree at 20° C. with an average correction at 20° at the end of the column.

Column 1.—Glycerine used.

Column 2.—Specific gravity at 15.5° C.; Table II, column 3.

Column 3.—Specific gravity at 20° C. without glycerine expansion correction; Table II, column 4.

TABLE III.—DETERMINATION OF THE VALUE OF "B" IN THE FORMULA  $\frac{W}{C} \frac{1}{1 + a(t - 15.5)} + B(t - 15.5)$ .

$$"B" = \frac{(\text{Specific gravity at } 15.5^\circ) - \left( \frac{W}{C} \frac{1}{1 + a(t - 15.5)} \right)}{(t - 15.5)}$$

Glycerine.	Specific gravity at 15.5° C.	Specific gravity at 20° without glycerine expansion correction taken from Table II, Column 5.	Column 2 minus Column 3.	Value of "B" at 20° C.	Specific gravity at 25° without glycerine expansion correction taken from Table II, Column 6.	Column 2 minus Column 6.	Value of "B" at 25° C.	Specific gravity at 30° without glycerine expansion correction taken from Table II, Column 9.	Column 2 minus Column 9.	Value of "B" at 30° C.
(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).	(11).
A.....	1.25465	1.25190	0.00275	0.000610	1.24878	0.00587	0.000618	1.24564	0.00901	0.000621
B.....	1.25736	1.25461	0.00275	0.000610	1.25149	0.00587	0.000618	1.24835	0.00901	0.000621
C.....	1.26012	1.25736	0.00276	0.000613	1.25423	0.00589	0.000620	1.25108	0.00904	0.000623
D.....	1.26026	1.25749	0.00277	0.000616	1.25438	0.00588	0.000619	1.25126	0.00900	0.000621
E.....	1.26077	1.25800	0.00277	0.000616	1.25491	0.00586	0.000617	1.25176	0.00901	0.000621
F.....	1.26135	1.25858	0.00277	0.000616	1.25548	0.00587	0.000618	1.25233	0.00902	0.000622
G.....	1.26177	1.25899	0.00278	0.000618	1.25589	0.00588	0.000619	1.25273	0.00904	0.000623
H.....	1.26238	1.25965	0.00273	0.000601	1.25659	0.00578	0.000610	1.25348	0.00890	0.000614
I.....	1.26312	1.26037	0.00275	0.000610	1.25728	0.00584	0.000615	1.25416	0.00896	0.000618
J.....	1.26340	1.26067	0.00273	0.000601	1.25759	0.00581	0.000612	1.25448	0.00892	0.000615
K.....	1.26368	1.26092	0.00276	0.000613	1.25783	0.00585	0.000616	1.25469	0.00899	0.000620
L.....	1.26418	1.26138	0.00280	0.000622	1.25829	0.00589	0.000620	1.25515	0.00903	0.000623
Average.....				0.000612			0.000617			0.000622

Columns 6, 7 and 8.—Specific gravity at 25° without glycerine expansion correction and so on as described for columns 3, 4, and 5 with an average correction per degree at 25° C. at the end of column 8.

Column 4.—Coefficient of expansion of glycerine taken as 0.00061 at 20° C.

Column 5.—Specific gravity determined at 20° and calculated to specific gravity at 15.5°, using 0.00061 as the coefficient of expansion at

TABLE IV.—SPECIFIC GRAVITY OF GLYCERINE DETERMINED AT 20°, 25° AND 30° AND CALCULATED TO 15.5° ACCORDING TO THE FORMULA:

$$\text{Specific gravity at } 15.5^\circ = \frac{W}{C} \frac{1}{1 + a(t - 15.5)} + B(t - 15.5)$$

Glycerine.	Average expansion specific correction taken from Table II, Column 5.	Specific gravity at 20° without glycerine expansion correction taken from Table III, Column 5.	Glycerine expansion correction at 20° and calculated to sp. gr. at 15.5°.	Specific gravity at 25° without glycerine expansion correction taken from Table II, Column 7.	Glycerine expansion correction at 25° and calculated to sp. gr. at 15.5°.	Specific gravity at 30° without glycerine expansion correction taken from Table II, Column 9.	Glycerine expansion correction at 30° and calculated to sp. gr. at 15.5°.
(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).
A.....	1.25465	1.25190	0.00061 × 4.5	1.25465	1.24878	0.000615 × 9.5	1.24562
B.....	1.25736	1.25461	0.00061 × 4.5	1.25736	1.25149	0.000615 × 9.5	1.25733
C.....	1.26012	1.25736	0.00061 × 4.5	1.26011	1.25423	0.000615 × 9.5	1.26007
D.....	1.26026	1.25749	0.00061 × 4.5	1.26024	1.25438	0.000615 × 9.5	1.26022
E.....	1.26077	1.25800	0.00061 × 4.5	1.26075	1.25491	0.000615 × 9.5	1.26075
F.....	1.26135	1.25858	0.00061 × 4.5	1.26133	1.25548	0.000615 × 9.5	1.26132
G.....	1.26177	1.25899	0.00061 × 4.5	1.26174	1.25589	0.000615 × 9.5	1.26173
H.....	1.26238	1.25965	0.00061 × 4.5	1.26240	1.25659	0.000615 × 9.5	1.26243
I.....	1.26312	1.26037	0.00061 × 4.5	1.26313	1.25728	0.000615 × 9.5	1.26312
J.....	1.26340	1.26067	0.00061 × 4.5	1.26342	1.25759	0.000615 × 9.5	1.26343
K.....	1.26368	1.26092	0.00061 × 4.5	1.26367	1.25783	0.000615 × 9.5	1.26367
L.....	1.26418	1.26138	0.00061 × 4.5	1.26415	1.25829	0.000615 × 9.5	1.26413

Columns 9, 10 and 11.—Specific gravity at 30° C. without glycerine expansion correction and so on as described for columns 3, 4 and 5, with an average correction per degree at 30° C. at the end of column 11.

Table IV:

that temperature for comparison with the specific gravity when determined at 15.5° C.

Columns 6, 7 and 8.—Specific gravity at 25° without glycerine expansion correction and so on as described for columns 3, 4 and 5.

Columns 9, 10 and 11.—Specific gravity at 30° C. without glycerine expansion correction and so on as described for columns 3, 4 and 5.

#### SUMMARY.

In consideration of the importance connected with obtaining a true value for the thermal coefficient of expansion of glycerine, the greatest care was observed in every detail of the foregoing work. It may appear superfluous to report the determinations of the specific gravity to the fifth decimal place, but as they agreed so closely at that point when different pycnometers were used in doing duplicate determinations, it seemed better to show the actual results obtained, which also shows the degree of accuracy that entered into the work.

From the foregoing results, it is apparent that the published values for the thermal coefficient of expansion of dynamite glycerine are not true between 15.5° and 30° C.

Taking the average coefficients of expansion from Table II as 0.000612 at 20° C., 0.000617 at 25° C. and 0.000622 at 30° C., which are in round numbers 0.00061 at 20°, 0.000615 at 25° and 0.00062 at 30°, and applying them as shown in Table IV, the determinations show very close agreement with the determinations made at 15.5° C.

The idea in using the round numbers 0.00061, 0.000615 and 0.00062 as the coefficients of expansion for glycerine is that they are easily remembered and are accurate enough for all practical purposes.

EASTERN LABORATORY.

E. I. DUPONT DE NEMOURS POWDER CO.,  
September 1, 1909

### FLASH, FIRE AND EXPLOSION TESTS ON MIXTURES OF CARBON TETRACHLORIDE AND NAPHTHA.

By EDW. A. BARRIER.

Received September 2, 1909.

The frequent occurrence of fires, explosions, or both, resulting from the wide-spread use of naphtha in removing oil from textile materials or metal goods in factories, makes it a matter of serious concern that no suitable, non-inflammable substitute has as yet been found. Of late years carbon tetrachloride has received some attention in this connection, but its comparatively high cost has barred its use except in a very limited way. Recent reductions in the price of this material, however, and the fact that a certain percentage of naphtha can be added without rendering the mixture inflammable have brought the cost of such a mixed solvent down to a point where it can be used in many cases, especially, if the spent solvent is reclaimed by distillation.

The importance of this matter led to the follow-

ing series of experiments which were undertaken with the object of determining how great a percentage of naphtha, of various gravities, could be added to carbon tetrachloride, and still leave the mixture free from fire and explosion hazard.

Four samples of commercial naphtha, labeled as below, were obtained from a petroleum refiner for the tests. The specific gravities of these samples were found to be as follows:

	Labeled.	Sp. gr. found.
I.....	54° B $\phi$ .	0.7556-55 $\frac{1}{2}$ ° B $\phi$ .
II.....	62° B $\phi$ .	0.7251-63° B $\phi$ .
III.....	Motor gasoline, 68-72° B $\phi$ .	0.6982-70 $\frac{1}{2}$ ° B $\phi$ .
IV.....	73-76° B $\phi$ .	0.6811-75 $\frac{1}{2}$ ° B $\phi$ .

Distillation tests of these naphthas were made with the following results:

Gravity.	80-100°.	100-110°.	110-120°.	120-130°.	130-140°.
55 $\frac{1}{4}$ °	.....	.....	.....	17.0 cc. <sup>1</sup>	20.5 cc.
63 $\frac{1}{2}$ °	12.5 cc.	23.5 cc.	22.0 cc.	18.0 cc.	8.0 cc.
Gravity.	140-150°.	150-160°.	160-170°.	170-180°.	Above 180°.
55 $\frac{1}{4}$ °	14.0 cc.	11.0 cc.	9.5 cc.	7.0 cc.	17.0 cc.
63 $\frac{1}{2}$ °	16.0 cc. above 140°				
Gravity.	50-60°.	60-70°.	70-80°.	80-90°.	
70 $\frac{1}{2}$ °	2.0 cc. <sup>3</sup>	5.0 cc.	19.0 cc.	24.5 cc.	
75 $\frac{1}{2}$ °	3.5 cc.	23.0 cc.	24.0 cc.	18.0 cc.	
Gravity.	90-100°.	100-110°.	110-115°.	Above 115°.	
70 $\frac{1}{2}$ °	21.0 cc.	11.0 cc.	4.0 cc.	14.0 cc.	
75 $\frac{1}{2}$ °	13.0 cc.	5.5 cc.	12.0 cc. above 110°		

#### FLASH AND FIRE POINT TESTS.

The flash and fire point tests were made in the open cup of the New York State Board of Health tester, and also in some cases, in a six-inch evaporating dish. No difficulty was experienced in determining the flash points of the various mixtures, but in no case could a definite fire point be found. On raising the temperature from the flash point, the liquid would usually flash and burn for one or two seconds, and then go out of itself. A further raising of the temperature resulted in some cases in lengthening the time of burning, and, in other cases, in decreasing the time of burning. Repeated tests of the same mixture, however, gave reasonably concordant results.

The mixtures containing the limiting amounts of naphtha, which are later stated to be reasonably safe, were tested in an evaporating dish, in addition to the open cup, as it was thought that this form of container with a large evaporating area was more comparable to the ordinary open bath frequently found in works.

On account of the absence of a true fire point the temperature was gradually raised from the flash point to the boiling point, and the observations recorded below were taken.

The results are given in the following table:

<sup>1</sup> Distillation began at 123°.

<sup>2</sup> Distillation began at 85°.

<sup>3</sup> Distillation began at 55°.

Kind of naphtha and flash-point.	Mixture tested.	Flash-point of mixture.	Observations.		Remarks.
			Temp.	Time of burning, sec.	
55½° Bé. 8° C.	50 per cent. naphtha and 50 per cent. tetrachloride.....	.....	.....	..	Did not flash at any tempera- ture.
	60 per cent. naphtha and 40 per cent. tetrachloride.....	35° C.	.....	..	Did not flash at temperatures above the flash point.
	70 per cent. naphtha and 30 per cent. tetrachloride.....	28° C.	45° C. 55° C.	4 6	Above 55° C. the mixture would not burn.
	80 per cent. naphtha and 20 per cent. tetrachloride.....	24° C.	35° C. 45° C.	5 8	Increasing the temperature ap- peared to have no appreciable effect.
63° Bé. —12° C.	40 per cent. naphtha and 60 per cent. tetrachloride.....	38° C.	.....	..	On raising temperature mix- ture would not flash.
	50 per cent. naphtha and 50 per cent. tetrachloride.....	18° C.	35° C. 45° C.	3 5	Further increase of tempera- ture decreased the time of burning.
	55 per cent. naphtha and 45 per cent. tetrachloride.....	10° C.	25° C. 35° C.	1 5	Further increase of tempera- ture appeared to have no ap- preciable effect.
	60 per cent. naphtha and 40 per cent. tetrachloride.....	0° C.	25° C. 35° C. 45° C. 70° C.	3 10 20 ..	Burned continuously until ex- tinguished.
70½° Bé. Below —18° C.	30 per cent. naphtha and 70 per cent. tetrachloride.....	—5° C.	25° C. 35° C.	1 2	At higher temperature would not burn.
	40 per cent. naphtha and 60 per cent. tetrachloride.....	—11° C.	25° C. 35° C.	10 15	Further increase of tempera- ture appeared to decrease time of burning.
	50 per cent. naphtha and 50 per cent. tetrachloride.....	Below —18° C.	0° C. 25° C. 35° C.	2 10 ..	Burned continuously until ex- tinguished.
	30 per cent. naphtha and 70 per cent. tetrachloride.....	—11° C.	10° C. 25° C. 35° C. 45° C.	1 2 5 8	Further increase of tempera- ture appeared to decrease time of burning.
75½° Bé. Below —18° C.	40 per cent. naphtha and 60 per cent. tetrachloride.....	Below —18° C.	0° C. 25° C. 35° C. 45° C.	3 12 15 ..	Burned continuously until ex- tinguished.

## EXPLOSION TESTS.

The explosion tests were carried out in a specially constructed box, 10"×11"×15" (see Fig. 1), heavily built, and made air-tight. The cover was provided with a tongue on the under side, which fitted into a channel placed on the upper, inside edges of the box. The channel was partly filled with water, thus making an air-tight seal. The box was also provided with an inlet pipe at the top of one end, and an outlet pipe at the bottom of the other end, both of 1/4" bore. Two copper bars passing through

the outlet end of the box served as terminals for making connections with an electric circuit.

The vapor was introduced into the box by connecting the outlet pipe with a suction pump, and the inlet pipe with an Erlenmeyer flask, fitted with a rubber stopper and two glass tubes, one of which dipped into the mixture to be tested. The amount of vapor sucked into the box was regulated by using a constant flow of water through the suction pump, and varying the time suction was applied. When the desired amount of vapor



had been drawn into the box, the suction pump and flask were disconnected, and the terminals were wired to an electric circuit. The charge was then fired by "short-circuiting" a one ampere fuse placed on the inside of the box.

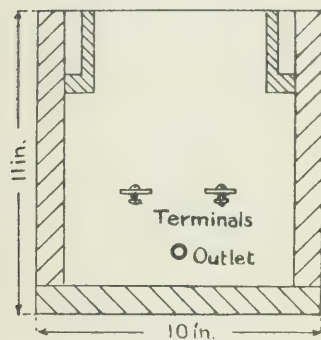


FIG. 1.

M.M.Jr.

Before the final series of tests were run a number of preliminary experiments were made with pure naphtha, in which the time of application of the suction was varied, in order to determine within what range the maximum explosive

effect could be obtained. This was found to be from 30 seconds to four minutes, and this range, except in certain cases where no explosion could be obtained, was accordingly used in the series of tests which appear in the following tables:

TABLE I 55 $\frac{1}{4}$ ° BÉ. NAPHTHA. TEMPERATURE 20°.

Mixture.	Time suction was applied.	Height cover was lifted.	Remarks.
Pure naphtha .....	1 min.	Did not move	No explosion.
" .....	2 min.	"	"
" .....	4 min.	"	"
" .....	8 min.	"	"

TABLE II 63° BÉ. NAPHTHA. TEMPERATURE 20°.

Mixture.	Time suction was applied.	Height cover was lifted.	Remarks.
Pure naphtha .....	1 min.	Did not move.	No explosion.
" .....	2 min.	"	"
" .....	4 min.	"	"
" .....	8 min.	"	"

All of the above tests with the 70 $\frac{1}{2}$ ° naphtha were repeated using a temperature of 38°, with the idea of simulating conditions which occur in summer. Practically the same results were obtained as with the lower temperature, with the exception that the same explosive effect was obtained in a shorter time.

From an examination of the tables, it will be

III. 70 $\frac{1}{2}$ ° BÉ. NAPHTHA TEMPERATURE 21°.

Mixture.	Time suction was applied.	Height cover was lifted.	Remarks.
Pure naphtha .....	1 min.	7 ft.	No flame visible.
" .....	2 min.	2 $\frac{1}{2}$ ft.	Considerable flame, evident excess of vapor.
50 per cent. CCl <sub>4</sub> and 50 per cent. naphtha .....	1 min.	Did not move.	No explosion.
" .....	2 min.	"	"
" .....	4 min.	"	"
40 per cent. CCl <sub>4</sub> and 60 per cent. naphtha .....	1 min.	"	"
" .....	2 min.	"	"
" .....	4 min.	Very slight movement.	"
30 per cent. CCl <sub>4</sub> and 70 per cent. naphtha .....	1 min.	"	"
" .....	2 min.	1 $\frac{1}{2}$ ft.	"
" .....	4 min.	1 $\frac{1}{4}$ ft.	Green flame, evident excess of vapor.

IV. 75 $\frac{1}{2}$ ° BÉ. NAPHTHA TEMPERATURE 21°.

Mixture.	Time suction was applied.	Height cover was lifted.	Remarks.
Pure naphtha .....	30 sec.	Did not move.	No flame visible.
" .....	1 min.	6 ft.	Some flame visible.
" .....	2 min.	2 ft.	Considerable flame, evident excess of vapor.
" .....	4 min.	1 ft.	"
60 per cent. CCl <sub>4</sub> and 40 per cent. naphtha .....	1 min.	"	"
" .....	2 min.	Did not move.	"
" .....	4 min.	"	"
50 per cent. CCl <sub>4</sub> and 50 per cent. naphtha .....	1 min.	"	"
" .....	2 min.	Moved slightly.	"
" .....	4 min.	2 inches.	"
40 per cent. CCl <sub>4</sub> and 60 per cent. naphtha .....	1 min.	3 inches.	"
" .....	2 min.	9 inches.	"
" .....	4 min.	1 $\frac{1}{2}$ ft.	"
30 per cent. CCl <sub>4</sub> and 70 per cent. naphtha .....	1 min.	4 inches.	"
" .....	2 min.	2 $\frac{1}{2}$ ft.	"
" .....	4 min.	2 ft.	Flame visible, evident excess of vapor.

seen that no explosion could be obtained with the  $55\frac{1}{4}^{\circ}$  and the  $63^{\circ}$  naphthas. This is in line with what experience has generally shown, namely, that there is but slight explosion hazard connected with the ordinary use, at the usual room temperatures, of naphthas having gravities around  $60^{\circ}$  or below.

#### CONCLUSIONS.

As a result of these tests the following conclusions seem warranted:

(1) That a certain percentage of naphtha can be added to carbon tetrachloride and still leave the mixture free from fire and explosion hazard.

(2) That the percentage which can be safely added varies with the gravity of the naphtha.

(3) That  $55^{\circ}$  naphtha at ordinary room temperatures is practically free from explosion hazard, but in order to be reasonably safe from fire hazard, it should contain at least 30 per cent. of carbon tetrachloride.

(4) That  $63^{\circ}$  naphtha at ordinary room temperatures presents but slight explosion hazard, but in order to be reasonably safe from fire hazard, it should contain at least 45 per cent. of carbon tetrachloride.

(5) That  $70^{\circ}$  naphtha in order to be safe from explosion hazard should contain at least 50 per cent. of carbon tetrachloride, and to be reasonably safe from fire hazard should contain 60 per cent.

(6) That  $76^{\circ}$  naphtha to be safe from explosion hazard should contain at least 60 per cent. of carbon tetrachloride, and to be reasonably safe from fire hazard should contain 70%.

The above statements apply, naturally, only to naphthas which show approximately the same results on distillation, especially with respect to the lower boiling fractions, as those tested. The expression "reasonably safe from fire hazard" is used advisedly, since the above mixtures, while possessing but little fire hazard in open containers, will burn if spread out over a considerable area, on any other readily combustible material such as cotton waste. The percentages of naphtha, stated in each case, are limiting ones, and good practice would call for an additional 5 per cent. of carbon tetrachloride in order to allow some factor of safety.

#### THE MOISTURE DETERMINATION AS APPLIED TO CEREALS.

By SHERMAN LEAVITT.

Received October 5, 1909.

The object of this investigation was to find out if a variation of one or two degrees from the standard temperature of one hundred degrees centigrade in

the determination of moisture content of cereals would have an appreciable effect on the percentage of moisture obtained under otherwise similar conditions. These conditions were that all the determinations be made in a partial vacuum with a gentle current of air passing through and that the drying be continued until the sample ceased to lose and commenced to increase in weight, it being generally assumed that cereals are dry when they begin to increase in weight on further heating.

In the fall of 1907, the writer had occasion to make moisture determinations on a large number of samples of wheat. Quite a number of these samples, unknown to the writer at the time, had been accidentally duplicated by another chemist. The results obtained by him on the same wheats were found to be in general about two per cent. higher on the basis of the fresh substance than ours. As this difference in results was fairly constant and was material in amount, the present investigation was started to determine, if possible, the cause for this divergence.

A cylindrical, heavy, brass, vacuum oven which was constructed with a water jacket was used. The oven was provided with a vacuum gauge and a thermometer, standardized by the Bureau of Standards, for which the correction was known. During the drying process, a slow current of air, dried by passing through strong sulphuric acid, was drawn over the samples, maintaining meanwhile a vacuum of about twenty-four inches of mercury. The samples were different varieties of wheat, ground to pass a one millimeter sieve, being well mixed and kept in tightly stoppered bottles. The experiment was devised and carried out so as to have as nearly as possible only one variable, *i. e.*, the temperature of the interior of the oven. As stated before, the end point of the drying operation was when the samples ceased to lose weight and showed a tendency to increase in weight. This was generally accomplished in five hours, the time being taken as soon as the oven had reached the desired temperature in the partial vacuum and current of air. The temperature was changed by the following simple conditions: When the oven was unprotected by asbestos covering and heated by an ordinary bunsen burner, with the oven jacket partially filled with tap water, a very even temperature of  $97^{\circ}$  Centigrade was maintained. By using a larger gas burner of the gridiron type and asbestos covering for the oven and flame, temperatures of  $98^{\circ}$  and  $99^{\circ}$  could be obtained under the standard vacuum conditions of twenty-four inches of mercury and two or three bubbles of air to the second passing through the oven.

It is interesting to note at this point that the temperature of the interior of the oven, as indicated by the standard thermometer, never reached  $100^{\circ}$  by

a whole degree.<sup>1</sup> The thermometer was always kept at the same depth of immersion in the bath, which was about at the point on the scale corresponding to 97°, so that practically the whole mercury column was immersed. Any correction on the thermometer was made according to the printed rules of the Bureau of Standards certificate accompanying the thermometer.

By using a mixture containing 20 per cent. of glycerine by volume (the percentage being determined experimentally) in the water jacket, an even temperature of 100° C. was obtained. Temperatures of 101° and 102° C. were obtained in a similar oven which was without the water jacket compartment and was heated directly by the gas flame, the temperature being regulated by a thermostat. This type of oven had been used in obtaining the high results referred to in the first part of this paper.

Circular, flat, aluminum dishes, with tightly fitting covers, were used to hold the samples (2 gram samples) so that the dry and very hygroscopic grain could not absorb an appreciable amount of moisture while on the pan of the balance during weighing. In Table I the results have been arranged so as to show the divergence between duplicates and the corresponding results for each sample at different temperatures:

TABLE I.

No. of sample.	(1) 97°.		(2) 98°.		(3) 99°.		(4) 100°.		(5) 101°.	
	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.
1993	8.15 8.19	8.17	8.11 8.32	8.22	8.69 8.82	8.75	9.37 9.43	9.40	9.72 9.78	9.75
1994	8.07 8.05	8.06	8.77 8.73	8.75	9.04 8.98	9.01	9.61 9.62	9.62	9.78 9.84	9.81
1995	9.12 9.00	9.06	8.85 9.08	8.97	9.44 9.40	9.42	9.83 9.82	9.83	10.45 10.54	10.50
2151	7.09 8.69	*	8.23 8.41	8.32	8.37 8.53	8.45	9.02 9.12	9.07	9.34 9.41	9.37
2152	8.29 8.28	8.29	7.90 7.62	7.76	8.66 8.58	8.62	9.31 9.41	9.36	9.47 9.36	9.41
2154	8.29 8.42	8.35	8.09 8.12	8.11	8.59 8.75	8.67	9.23 9.33	9.28	9.59 9.59	9.59
2155	8.36 8.44	8.40	8.50 8.61	8.55	8.77 8.73	8.75	9.46 9.28	9.36	9.65 9.61	9.63
2156	7.58 8.03	*	8.09 8.25	8.17	8.40 8.56	8.48	9.04 9.14	9.09	9.60 9.59	9.60
2176	8.18 7.85	*	8.22 8.38	8.30	8.51 8.40	8.45	9.16 9.16	9.16	9.51 9.53	9.52

\* Duplicates not sufficiently close to average.

EXPLANATION OF TABLE I.

All results were taken at point where samples commenced to increase in weight.

Columns (1), (2) and (3), corresponding to temperatures 97°, 98° and 99° C., were obtained in the oven with water in the jacket.

Column (4), corresponding to 100° C., was obtained

<sup>1</sup> It has been suggested that the expansion of the bulb of the thermometer in the vacuum was responsible for this one degree low reading of the thermometer. The writer, however, is of the opinion that the loss of heat, due to radiation because of an air leak in the oven, which was afterwards discovered, was responsible for it, because the oven failed to reach the boiling point of water when there was very little vacuum on.

in the same oven with a 20 per cent. by volume solution of glycerine and tap water.

Column (5), corresponding to 101° C., was obtained in the hot air vacuum oven regulated by a thermostat.

Column (6), not given because exact figures were mislaid or lost, corresponding to 102° C. Gave results all above 11 per cent. and approximating the high results previously referred to.

Table II has been arranged so as to show the effect of heating at 100° C. for different lengths of time:

TABLE II.  
All temperatures 100° C.

No. of sample.	(a) 3½ hours.		(b) 4½ hours.		(c) 5 hours.			(d) Over 5 hours.	
	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.	Per cent. H <sub>2</sub> O.	Aver. age.		Per cent. H <sub>2</sub> O.	Aver. age.
1993	9.24 9.32	9.28	9.37 9.43	9.40	9.37 9.43	9.40	Sample increased in weight.	9.40	9.40
1994	9.42 9.45	9.44	9.61 9.62	9.62	9.61 9.62	9.62	Sample increased in weight.	9.62	9.62
1995	9.09 9.10	9.09	9.82 9.82	9.83	9.96 9.91	9.94	Sample increased in weight.	9.94	9.94
2151	9.00 8.87	8.93	9.00 9.12	9.07	9.30 9.17	9.24	Sample increased in weight.	9.24	9.24
2152	9.19 9.24	9.21	9.31 9.41	9.36	9.41 9.41	9.36	Sample increased in weight.	9.36	9.36
2154	9.16 9.08	9.12	9.23 9.33	9.28	9.23 9.33	9.28	Sample increased in weight.	9.28	9.28
2155	9.05 8.93	9.00	9.46 9.28	9.36	9.50 9.37	9.42	Sample increased in weight.	9.42	9.42
2156	8.72 8.71	8.72	9.04 9.14	9.09	9.16 9.13	9.15	Sample increased in weight.	9.15	9.15
2176	8.77 8.88	8.82	9.16 9.16	9.16	9.29 9.32	9.31	Sample increased in weight.	9.31	9.31

EXPLANATION OF TABLE II.

Temperature constant at 100° C., weighings taken at different periods of time, giving some comparisons of length of time of heating on fresh samples in oven jacketed with 20 per cent. by volume solution of glycerine and tap water. We notice that the results in column (c), Table II, agree very well with the results in column (4), Table I, showing that practically all of the moisture had been driven off in from four and one-half to five hours' heating at 100° C.

From these results we conclude that a variation of one degree either below or above 100° C. will make a marked and appreciable difference in the moisture results on wheat, and probably would with other cereals as well. It is usually customary to calculate all analytical results on cereals to the *water-free basis* for comparison; hence, it is evident that the moisture determination is of the highest importance, as an error in this determination will change all of the other analytical results.

No attempt is made in this article to explain why it is that a long slow drying, at a lower temperature than 100° C., did not give the same results as at 100° C. Theoretically, we should expect the same results, but in the hands of the writer they barely gave within two per cent. of the same results and further heating showed quite a rapid increase in weight of



all samples examined, especially at the lower temperatures.

This work was carried out in the fall and winter of 1907, in the laboratory of Vegetable Physiological Chemistry of the Bureau of Chemistry of the U. S. Department of Agriculture, at Washington, D. C. The writer wishes to make special acknowledgment to Dr. J. Arthur LeClerc, chief of the above laboratory, for his many kindnesses and courtesies and for many valuable suggestions in connection with this study. The writer is also indebted to Professor Charles A. Mooers, of this station, for reading and criticizing this paper.

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THE UNIVERSITY OF MISSOURI.]

## THE GLYCOGEN CONTENT OF BEEF FLESH.

(FIRST PAPER.)

By P. F. TROWBRIDGE AND C. K. FRANCIS.

Received July 6, 1909.

*Consideration of the Problem.*—In connection with the "Use of Food" experiment with beef animals now in progress at the Agricultural Experiment Station of Missouri, one of the points to be studied is the variation in the composition of the flesh as affected by feed, age or breed of the animal. It was thought quite probable that variation in quantity of feed would particularly influence the glycogen content. With this in view, an experiment was outlined to study the glycogen content of certain parts of the steers to be slaughtered. Since the animals were to be slaughtered under similar conditions as to length of time off feed, it was possible to secure the samples under quite uniform conditions. The liver was selected as an organ especially to be examined, and for a sample of the flesh it was decided to take a sample from the lean clod muscle of the shoulder, as this could be obtained without seriously mutilating the carcass.

*Method of Securing and Preparing the Samples.*—The following method was used in securing and preparing the samples for analysis: The animals were given their regular feed at 6 A.M. and were knocked in the head at about 8.30 A.M. A chain was wrapped around the hind legs, the carcass hoisted from the floor, and the animal bled thoroughly. As soon as the bleeding was complete, and before the animal was lowered to the floor, a piece of the hide was stripped from over the shoulder of the left side and about one kilo of lean clod muscle removed and taken at once to the laboratory. There, as rapidly as possible, it was put through an Enterprise meat grinder three times with thorough mixing between each grinding. A sample was taken immediately from this

ground meat for determination of all the analytical data desired, including the glycogen determination.

At the slaughter-house the work of dressing the carcass was carried on as rapidly as was possible, securing and weighing the necessary samples, taking notes, etc. As soon as the contents of the abdominal cavity were removed, the liver from which the gall bladder had been separated, was weighed and sent to the laboratory, where it was immediately ground and mixed in the same manner as the sample of flesh. The samples were weighed out for the analyses as rapidly as possible. This work has been carried on with fifteen animals slaughtered during the past two years, under conditions as nearly uniform as it has been possible to make them. At first several hours elapsed from the time the sample was removed from the carcass until the portions were weighed out and treated with alkali. Later it was found possible to reduce this time very materially. This will be noted in the tables and in the discussion of the data.

*Method of Analysis as Adopted.*—With the first animal different methods<sup>1</sup> were studied and compared with the adoption of the following method as the most satisfactory procedure.<sup>2</sup>

*Solution of the Sample.*—Weigh out by difference in triplicate, about 25 grams of the finely ground and thoroughly mixed sample. Place the sample in 400 cc. beakers, mixed with 50 cc. of strong potassium hydroxide<sup>3</sup> solution. Cover the beaker with a watch-glass and digest on the water bath for two hours, with occasional stirring. At the end of the two hours, dilute to approximately 200 cc. with cold water.

*Separation of the Glycogen.*—Add to the solution an equal volume of 95 per cent. alcohol, cover with the watch-glass and set aside for 10 or 12 hours, in order that precipitation of the glycogen may be complete. Decant the supernatant liquid through a folded filter (S. & S. No. 588, 18½ cm.), allowing the glycogen to remain in the beaker and wash by decantation with 66 per cent. alcohol (2 vol. of 95 per cent. alcohol with 1 vol. of water) until the glycogen is white, or nearly so. Usually about four washings are required. Transfer the washed precipitate from the beaker to the filter and wash two or three times with 66 per cent. alcohol. The solution filters slowly and the funnel should be covered with a watch-glass to prevent excessive evaporation. The albuminous substance present retards the filtration if permitted to dry on the paper. If the washing by decantation

<sup>1</sup> Pflüger, *Arch. f. d. Gesamte Physiologie*, 95 and 96 (1903); Allen, *"Organic Analysis,"* 1, 284; 2, 275 (1898).

<sup>2</sup> Mr. L. F. Shackell, now assistant in the physiological laboratory of St. Louis University School of Medicine, was placed in charge of the laboratory work during the first part of this work and credit is hereby given him for his assistance in securing the data here presented.

<sup>3</sup> 150 grams of pure KOH free from carbonate to every 100 cc. of water.



is not made nearly complete, it will be difficult to obtain the glycogen free from the coloring matter.

*Purification of the Glycogen.*—After the washing is completed, close the bottom of the funnel by a piece of rubber tubing and a pinchcock. Fill the funnel with warm water, cover with the watch-glass and let stand two or three hours, or overnight. Remove the pinchcock and allow all of the solution to pass through the filter into a beaker. Close the funnel with the pinchcock and fill with warm water as before. Allow this water to remain in the funnel for one hour and then filter as before. At first the glycogen solution appears quite turbid. This washing with warm water should be continued until the filtrate becomes perfectly clear. To the solution of glycogen in water, add a double volume of 95 per cent. alcohol and let stand overnight to complete the reprecipitation of the glycogen. Filter and wash as before with 66 per cent. alcohol.

*Quantitative Estimation of the Glycogen.*—If desired, the last filtration can be made through tared Gooch crucibles and the weight of glycogen determined after drying to constant weight. This gives results that are approximately correct. A more satisfactory method, however, is to hydrolyze the glycogen with hydrochloric acid and determine the amount of the resultant glucose by means of Fehling's solution. This method proceeds as follows: The well washed precipitate of glycogen is dissolved on the filter as described above, collecting the filtrate in a 250 cc. measuring flask. The volume of the solution should be kept within 225 cc. Add 12.5 cc. of hydrochloric acid, specific gravity 1.19, and place the flask in a boiling water bath for three hours. When the contents of the flask are cooled make up to the mark with water and mix thoroughly.

By means of preliminary tests determine the amount of the glucose solution that can be used with 60 cc. of the mixed Fehling's solution. With a burette or pipette measure out in triplicate the amount of the glucose solution which the preliminary test has shown can be used with the 60 cc. of Fehling's solution. Neutralize the solution with potassium hydroxide and if the volume be less than 75 cc. add water to make about this amount. To this solution add 60 cc. of the previously mixed Fehling's solution. Heat rapidly to the boiling point over the naked flame and boil for exactly two minutes. Remove and add at once about 100 cc. of cold water. Allow the precipitate to settle completely, decant through a quantitative filter paper, transfer the precipitate to the filter paper and wash with hot water until the filter is free from alkali. Ignite the precipitate to cupric oxide, weigh and calculate the results to weight of glucose by means of Allihn's<sup>1</sup> tables. Calculate the

weight of glucose in the aliquot to the total sample, determining the amount of glycogen from the glucose by multiplying by 0.9<sup>1</sup> and calculate this result to per cent. in the fresh sample.

That the triplicate determinations agree reasonably well and also that the gravimetric determination gives approximately the same results as the method by hydrolysis is shown by the following results with steer No. 505, a fat yearling grade Hereford. Each result is from a separately weighed sample:

Lab. No.	Sample.	Method of hydrolysis, glycogen per cent.	Glycogen by weight, per cent.
822x	Liver.....	0.908	0.889
822y	Liver.....	0.951	0.889
822z	Liver.....	0.923	0.879
823x	Lean muscle.....	0.387	0.439
823y	Lean muscle.....	0.411	0.401
823z	Lean muscle.....	0.328	0.388

During the progress of the work it was found to be practicable to slaughter more than one animal at a time, therefore some of the animals were killed after a longer time off feed than were others. In the table below we tabulate the results, taking the average of the triplicate determinations arranged according to time off feed and in order of the amounts of glycogen in the liver:

Slaughtered within two or three hours after regular morning feed:

Lab. No.	Glycogen in Glycogen in liver, lean muscle,		Description of animal.
	per cent.	per cent.	
91102-3	3.803	0.663	No. 48, very fat short-horn, 4½ years old.
92102-3	2.337	0.697	No. 63, lean Jersey cow, 6 years old.
71251-2	1.210	0.243	No. 121, fairly fat Shorthorn, 3½ years old.
822-3	0.927	0.375	No. 505, fat yearling Hereford.
8122-3	0.820	0.309	No. 504, fat Hereford, 20 months old.

Slaughtered five or six hours after regular morning feed:

9252-3	0.965	0.569	No. 595, thin Hereford, 2 years old.
9152-3	0.913	0.416	No. 592, very thin Hereford, 23 months old.
8255-6	0.625	0.158	No. 503, thin Hereford, 11 months old.

Slaughtered about nine hours after regular morning feed:

92151	1.160	not det.	Jerry, very fat prize Hereford, 3 years old.
89102-3	0.284	0.140	No. 593, fairly fat Hereford, 18 months old.

The data are insufficient to draw any conclusions but it is possible to point out the probable factors, that may influence the glycogen content.

(1) It is quite possible the older the animal the greater the tendency to store the glycogen. All

<sup>1</sup> Methods of Analysis A. O. A. C., published as U. S. Dept. of Agriculture, Bureau of Chem., Bull. 107 (revised), p. 50.

<sup>1</sup>  $C_6H_{12}O_6 + H_2O = C_6H_{12}O_5$ .  
162 + 18 = 180.

of the animals 3 years old or over show more than one per cent. of glycogen in the liver.

(2) The condition (fatness) of the animal may favor the storing of glycogen. Our results are a little contradictory. No. 504 was very fat, No. 63 very thin, No. 503 not fat but in good thrifty condition, while No. 592 was extremely thin, approaching starvation. On the other hand, No. 48 was much fatter than No. 121, both being mature animals and being comparable in every respect except degree of fatness.

(3) The length of time that elapses after feeding before the animal is slaughtered seems to be a very important factor in determining the amount of glycogen that remains stored in the organs and muscles of the animal. If fatness is a favorable factor, Jerry should have shown fully as much glycogen as No. 48, but he does show less than one-third as much, having been slaughtered in the afternoon, eight hours off feed, while No. 48 was slaughtered in the morning, two hours off feed. On the other hand, Nos. 595 and 592 compare favorably with No. 505 and No. 504 as to glycogen content and age, but were much thinner and were slaughtered 3 or 4 hours later after feeding.

While we have just considered some of the factors that may influence the amount of glycogen that the animal stores up, it must not be overlooked that the time that elapses from the killing of the animal until the sample is digesting in the alkali may be the chief factor that influences the amount of glycogen found.

With our first animals slaughtered no exact record was taken of the time. The sample was always sent to the laboratory as soon as obtained and the chemist immediately went to work to prepare the sample for the analysis, thinking in this way to have all results comparable.

The failure of the results to establish any definite law and knowing how rapidly the acidity of flesh increases under similar conditions, led us to consider more carefully the element of time as measuring perhaps the amount of enzymatic reaction. With animals No. 63, No. 595 and Jerry, slaughtered February 22, 1909, the exact time was carefully noted.

No. 63, a thin Jersey cow six years old (not in milk), was killed at 8.55 A.M. The sample of lean muscle was received at the laboratory at 9.20. All weighings were completed and the alkali was added to the last sample at 10.10. The alkali was added to each sample as soon as it was weighed out, so that sample *x* had slightly less time for enzymatic hydrolysis than did *y*, and *y* had a corresponding less time than did *z*; sample *x* gave on analysis 0.714 per cent. glycogen and *y* gave 0.680 per cent. The beaker containing sample *z* was broken and at 3.26 P.M. the alkali was added to another sample *z*. In the meantime the ground meat had stood in a closed jar in the

laboratory; result of the analysis, 0.320 per cent. of glycogen, or less than one-half as much.

The liver from this same animal was received at 10.18 A.M. and the alkali was added to the last sample at 11.00 A.M. The glycogen found was *x*, 2.24 per cent.; *y*, 2.48 per cent.; and *z*, 2.29 per cent.

Steer No. 595 was killed at 11.15 A.M. The sample of lean muscle was received at the laboratory at 11.37 A.M. and the alkali was added to the last sample at 12.06 P.M. *x* gave 0.685 per cent. glycogen, *y* 0.526 per cent., and *z* 0.495 per cent. The liver was received at the laboratory at 12.06 P.M. and the alkali added to the last sample at 12.53 P.M. *x* gave 1.015 per cent., *y* 0.99 per cent., and *z* 0.89 per cent. glycogen. These results would seem to suggest that an appreciable amount of enzymatic hydrolysis may take place between the weighing out of the samples, although not confirmed by the results on No. 63, given just preceding or on the liver of Jerry, which follows.

Jerry was killed at 2.00 P.M. No sample of lean muscle was taken. The liver was received at the laboratory at 3.10 P.M. The grinding was delayed, as the mill was being used for another sample and had to be cleaned so that the alkali was not added to the last sample until 4.35 P.M. *x* gave 1.17 per cent., *y* 1.14 per cent. and *z* 1.17 per cent. glycogen.

If further work confirms the present results as to a rapid hydrolysis of the glycogen, it will show how utterly worthless the glycogen determination is for the detection of the presence of horse flesh.

*Low Temperature Checks Hydrolysis.*—A very fat sheep was killed at 2.45 P.M., March 21, 1908. The liver was removed at 3.20 P.M., and a portion was immediately sliced and frozen by covering with cracked ice and salt. When frozen, the ice and salt were brushed off and the liver was ground and thoroughly mixed. The temperature of the mixture remained below 0° C. The sample was placed in the ice-box and in the evening triplicate portions were weighed out and treated with the alkali, the temperature of the sample not exceeding 10° C.:

Alkali added to Sample 1 at 7.20 P.M., determination lost.

Alkali added to Sample 2 at 7.35 P.M., 1.84 per cent. glycogen found.

Alkali added to Sample 3 at 7.50 P.M., 1.81 per cent. glycogen found.

The main portion of the sample was kept in the ice-box until the next evening (3/22/08), temperature of sample was 9° C. Triplicate samples were again taken. Alkali was added to sample 1 at 7.20 P.M. 1.70 per cent. glycogen found.

Alkali was added to Sample 2 at 7.35 P.M., 1.71 per cent. glycogen found.

Alkali was added to Sample 3 at 7.50 P.M., 1.59 per cent. glycogen found.

The remainder of the sample was kept in the ice-box until the morning of (3/24/08), temperature of the sample did not exceed 10° C. Triplicate samples were taken:

Alkali was added to Sample 1 at 9.00 A.M., 1.73 per cent. glycogen found.  
Alkali was added to Sample 2 at 9.15 A.M., 1.76 per cent. glycogen found.  
Alkali was added to Sample 3 at 9.30 A.M., 1.71 per cent. glycogen found.

The following morning (3/25/'08) triplicate samples were taken, temperature did not exceed 6° C.

Alkali added to Sample 1 at 9.45 A.M., 1.65 per cent. glycogen found.  
Alkali added to Sample 2 at 10.00 A.M., 1.70 per cent. glycogen found.  
Alkali added to Sample 3 at 10.15 A.M., 1.73 per cent. glycogen found.

In the evening (3/25/'08) a sample was weighed out at a temperature of 8° C., which gave 1.67 per cent. glycogen. These results indicate that at 10° C. or lower no appreciable hydrolysis of the glycogen takes place. This problem is to be studied further during the ensuing year.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 175.]

### A SOURCE OF ERROR IN THE EXAMINATION OF FOODS FOR SALICYLIC ACID.

By H. C. SHERMAN.

Received September 20, 1909.

In testing foods for preservatives it is commonly assumed that a constituent volatile with steam, soluble in ether, capable of sublimation and crystallization, and giving a violet reaction with ferric chloride, must be salicylic acid. This assumption is, however, incorrect.

It has recently come to the attention of the writer that certain baked cereal products and prepared foods containing such products yield a constituent which shows all of these properties and which would therefore, upon ordinary examination, cause these foods to be reported as containing salicylic acid; but further study showed that the constituent in question did not come from the raw materials used but was developed during the baking process. Salicylic acid was in fact absent and the source of error was indicated by an examination of the literature of the ferric chloride test for salicylic acid and was fully demonstrated by experiment.

#### LITERATURE.

Brand found, in 1893,<sup>1</sup> that an extract of caramel malt gave a reaction with ferric chloride like that given by salicylic acid, and in a paper published the following year<sup>2</sup> cites Erich<sup>3</sup> and Munsche<sup>4</sup> as having made the same observation. In his paper of 1894,<sup>5</sup> Brand recorded the actual separation from such caramel malt of a crystalline substance, soluble in ether or water (much less soluble in cold water than hot), volatile with steam, capable of sublimation and reacting like salicylic acid with ferric chloride, but which did not give the red reaction of salicylic acid with Millon's reagent. By condensing the vapors given off during the roasting process in the manufacture

of a so-called malt coffee, extracting with ether, purifying and recrystallizing in different ways, Brand obtained the reacting substance in crystalline form both as leaflets and as needles. Brand named the substance "maltol," and showed that it had phenolic character and agreed with the formula  $C_8H_8O_3$ .

Kiliani and Bazlen<sup>1</sup> also prepared maltol in crystalline form, showed that it has an acid reaction, and studied its chemical behavior.

Will<sup>2</sup> studied its effect upon yeast.

Abraham<sup>3</sup> pointed out that dark-colored beers may readily contain maltol which, in the examination of the beer for preservatives, will behave like salicylic acid, both in steam distillation and extraction with ether, and give a marked violet coloration with ferric chloride. The ferric chloride reaction being thus inapplicable and the Millon reaction not suitable, Abraham recommended the Jorissen reaction.

This reaction for salicylic acid, proposed by Jorissen in 1882,<sup>4</sup> is as follows:

*Jorissen's Reaction.*—To the solution to be tested add 4 or 5 drops of a ten per cent. solution of potassium (or sodium) nitrite, 4 or 5 drops of acetic acid, 1 drop of a ten per cent. solution of copper sulphate and heat to boiling. In the presence of salicylic acid the solution turns reddish and with more than a very minute amount becomes blood-red. According to Jorissen phenol behaves in the same way but benzoic acid does not. Abraham found that maltol does not give this reaction and recommended it as the most reliable test for salicylic acid.

da Silva<sup>5</sup> used Jorissen's reaction among others.

Klett<sup>6</sup> recommends Jorissen's reaction for the detection of salicylic acid in substances containing citric acid.

Jorissen's reaction was one of those used by Portes and Desmoulières<sup>7</sup> as demonstrating the presence of small amounts of salicylic acid in strawberries.

Windsch,<sup>8</sup> investigating the natural occurrence of salicylic acid in fruits, and having obtained violet reactions with ferric chloride from raspberries and strawberries, adopted the Jorissen reaction to decide the question whether the reacting substance was actually salicylic acid.

Thus it is evident that the Jorissen reaction for the detection of salicylic acid is fairly well established in Europe.

<sup>1</sup> Ber., 27, 3115.

<sup>2</sup> Ztschr. ges. Brauw., 21, 307; abs. Ztschr. Unters. Nahr. Genussm., 1, 720.

<sup>3</sup> Journ. de Pharmacie, de Liège, 1898, 5, 173. Abstracted in Report Pharm. [3], 10, 347, and Ztschr. Unters. Nahr. Genussm., 1, 857.

<sup>4</sup> Bulletins de l'Académie Royale des Sciences, des Lettres, et des Beaux-arts de Belgique, 3rd series, 3, 259.

<sup>5</sup> Compl. rend., 131, 423 (1900); Bull. soc. chim. [3], 23, 795 (1900).

<sup>6</sup> Pharm. Centr., 41, 452; Ztschr. Unters. Nahr. Genussm., 4, 469.

<sup>7</sup> Annal. chim. analyt., 6, 401 (1901); Ztschr. Unters. Nahr. Genussm., 5, 468.

<sup>8</sup> Ztschr. Unters. Nahr. Genussm., 6, 447.

<sup>1</sup> Ztschr. f. d. ges. Brauw., 15, 303.

<sup>2</sup> Ber., 27, 806.

<sup>3</sup> Der Bierbrauer, 24, 465.

<sup>4</sup> Woch. f. Brauerei, 10, 739.



## EXPERIMENTAL.

Fifty grams of a prepared food consisting in part of a baked cereal product were mixed with water, acidulated with phosphoric acid and distilled with steam in an Erlenmeyer flask surrounded by oil heated to 120°-130°. Portions of distillate tested from time to time gave distinct violet reaction with ferric chloride, but no reddish color in Jorissen's test. The distillation was continued until the ferric chloride reaction was no longer obtained, when the total distillate measured 800 cc. When this was mixed and one-hundredth of it (8 cc.) tested with ferric chloride a distinct reaction like that of salicylic acid was obtained. That the reacting substance was not salicylic acid was shown by extracting thoroughly the other ninety-nine-hundredths of the distillate with ether, treating it as recommended by the Association of Official Agricultural Chemists<sup>1</sup> for the complete recovery of salicylic acid, subliming and testing the product obtained. Although this represented practically one hundred times as much of the substance as had last been tested and found to react with ferric chloride, no reaction whatever was obtained with the Jorissen test.

Comparative tests with known solutions indicated that in the writer's hands about twice as much salicylic acid is required for the Jorissen reaction as for the reaction with ferric chloride, whereas in the above case a distinct coloration was obtained with ferric chloride in a test representing 0.5 gram of the sample and no coloration when the Jorissen reaction was applied to a solution of about equal volume, which represented about 50 grams of the same sample, or about one hundred times as much. Hence if the reaction with ferric chloride in the first case had been due to salicylic acid there would have been present in the second case about 50 times as much as is required to give a distinct coloration with the Jorissen reaction. It is therefore abundantly evident that the substance which gave the violet reaction with ferric chloride was not salicylic acid. It was probably Brand's maltol or some very similar substance. The production of this substance is evidently due to the baking process or caramelization rather than to the presence of malt, though it may be produced more abundantly in the baking of malt than in the baking of flour.

When 25 grams of the brown outer crust of ordinary wheat bread (partly from "patent" and partly from "whole wheat" flour) were treated in the same manner as the prepared food described above, the distillate gave a distinct violet reaction with ferric chloride, though it was, of course, free from salicylic acid and did not give the Jorissen reaction.

It may also be noted that Abraham<sup>2</sup> obtained the

violet (maltol) reaction with ferric chloride from roasted coffee as well as from caramel malt.

## SUMMARY.

Maltol, an acid substance volatile with steam, soluble in ether, capable of sublimation, crystallizing sometimes in leaflets and sometimes in needles, and giving with ferric chloride the same violet color as salicylic acid has been shown to be formed in the baking or roasting of malt and the same or some similar substance is produced in the roasting of coffee and the baking of wheat bread.

Such a substance would be reported as salicylic acid when the present ferric chloride test is used, no matter how carefully the test be made and even if the precaution be taken to sublime the acid and a crystalline sublimate be obtained.

In order to avoid this source of error some reaction other than that with ferric chloride must be used for the detection of salicylic acid in foods. Jorissen's reaction, already well established in European literature, is not subject to the same source of error. In carrying out this reaction about 10 cc. of the liquid to be tested were used and to this were added 4 or 5 drops of ten per cent. potassium nitrite, 4 or 5 drops of fifty per cent. acetic acid, 1 drop of ten per cent. copper sulphate; the liquid, after shaking, was then heated to boiling and, if necessary, boiled for half a minute and allowed to stand one or two minutes for the red color to develop. Under these conditions 0.0005 gram of salicylic acid in 10 cc. water (1 : 200,000) gives a distinct reddish color, easily recognizable after a very little practice, especially on comparison with a blank test carefully made with the same amounts as the reagents. With larger amounts of salicylic acid an unmistakable blood-red color develops quickly on heating.

September 14, 1909.

## ADDRESSES.

A NEW STEP IN INDUSTRIAL EDUCATION.<sup>1</sup>

By ALLEN ROGERS, Ph.D.

At the present time when there is so much being said in the daily papers and magazines in regard to industrial education, it may be of interest to give an outline of what we are doing at Pratt Institute, and what we hope to do in the future.

Before undertaking, however, to describe what we are doing, I should like to point out two things that we do not attempt. In the first place we are not a trade school; that is, we do not claim to graduate men who are fitted to do only one kind of work. On the other hand we are far removed from the ordinary technical school or university. Although we may teach the same or similar subjects as given in trade or technical schools, we approach them in an entirely different manner, while the attitude of our students toward their work is also quite different. Our field, therefore, may be said to lie practically half way between the two.

In describing the aims of this course in Applied Chemistry,

<sup>1</sup> Read at New Haven Meeting, American Chemical Society, July 1, 1908.

<sup>1</sup> Bull. 107 (Revised). Bur. Chem., U. S. Dept. Agriculture.

<sup>2</sup> Loc. cit.



I do not wish to give the impression that it is the only course given at Pratt Institute, for as a matter of fact, there are more than sixty other courses, many of them day courses, and others evening courses, in all of which there is an enrolment of over four thousand students, drawn from nearly every state in the Union, and from a number of foreign countries. It requires nine different buildings to house these classes, other buildings also being in process of construction.

Some idea of the importance of this type of education can be gathered from the fact that the institute, which Mr. Pratt founded only twenty years ago, started with twelve students, and has grown to the proportions mentioned above, and during these twenty years has given instruction to more than sixty thousand individuals.

It is a significant fact that Mr. Pratt did not, in his will, lay down any hard and fast rules for the Institute. The Trustees have, therefore, made changes in its courses and methods whenever they seemed necessary, but have never changed its purpose, though this is also in their power.

It is owing to this elastic condition of affairs and to the increased demand for young men with technical training that it was deemed advisable to introduce a course in Applied Chemistry; consequently in September, 1905, the new work was undertaken, at which time the writer accepted the position as Instructor in Industrial Chemistry, and was told to organize his course and equip his laboratory for practical instruction. This may seem like a very simple proposition but rest assured it was no small task.

Being an entirely new departure in this method of teaching the subject, there was no school which could be visited in order to gain any information. It was therefore a question of originality. And now after three years of experience it is with a great deal of satisfaction and pride that I wish to correct a statement which appeared in a recent issue of one of our prominent trade journals.

The article referred to in describing a certain English technical training school says:

"We ought to have had an institution of this kind in America, where we are rather vain of our practical way of handling things; but we have not, and it remains for an Englishman to establish in the heart of England the only real American idea school in the world. Therefore if the bright sons of far-sighted American manufacturers want a real education in their father's business, they must have it made in England."

That we have had, and continue to have, such a school in America, if not already known, let us trust will be made evident by the following remarks.

There is much truth in the analogy drawn by our director when he says:

"When boys are preparing to play a game of football they do not go into a lecture room and listen to a discussion of the best methods of playing the game, but rather get out on the field and try to produce the same conditions as nearly as possible to those they will meet when thrown into contest with their adversaries."

Consequently if we are to teach young men the methods employed in the manufacture of commercial products, we must bring them in as close relationship as possible to the actual working conditions, by which means they will learn as much of the how and the why in one week as they would by months of class-room instruction. Therefore, in arranging for this course in Industrial Chemistry the above belief has been put into practice, five miniature factories having already been installed. These factories are thoroughly equipped for manufacture on a fairly large scale, each plant being a unit in itself is worked independently of the others and occupies a floor space of fifteen by five feet.

They are as follows: Chemical works, soap factory, tannery,

dry color, paint and varnish works, bleaching, dyeing and print works.

In order to suit the needs of a large number of young men who cannot afford either the time or money for a four-year course with college requirements, the course has been made but two years in length. It is designed especially to give the necessary technical knowledge and practical training to those who desire to become foremen, superintendents or heads of departments in the important chemical industries.

As a preliminary to the applied side of his subject the student is given a training in general inorganic chemistry, organic chemistry, qualitative and quantitative analysis together with the necessary amount of physics, mathematics and mechanical training. The last two subjects extend over both years and include mechanics, strength of materials, steam and power transmission, carpentry, forge, foundry, machine work and design.

As it is not within the scope of this paper to dwell upon the details of the above-mentioned subjects, therefore, it will be best to leave them out of the discussion and pass on to the industrial training which begins in the second year.

In order to acquaint the student with commercial processes one hour each day is devoted to the study of general industrial chemistry, by which means he becomes familiar with the details involved in the various branches of industry, thus materially broadening his field of view, one of the principal objects being to show the relation which exists between them, and where one depends upon the other, at the same time bringing into prominence the value of chemical control and the stages in the numerous processes wherein chemical knowledge is not only beneficial, but absolutely essential. On completing each industry one or more trips are made to such factories as best illustrate the points which have been studied, thus more firmly fixing the knowledge gained by class-room instruction.

Furthermore, each student is required to write a complete description of the trip, which becomes a part of his record and is returned to him upon graduation.

The laboratory instruction connected with this course differs very greatly from that given in most schools, inasmuch as it is entirely practical, consisting of the analysis of such substances as gas, water, coal, lubricating oils, vegetable oils, animal oils, soaps, baking powder, foods, milk, sizes, pulp colors, dry colors, paint, varnish, steel, copper, brass and other alloys, boiler compounds, chrome liquor, tan barks, extracts, etc., etc.

Whether this method has any advantage over the one usually employed is an open question with strong arguments on both sides.

It is on our industrial work proper, however, that we place special emphasis, as it is through this method of training that we hope to prepare young men to fill the positions that have been mentioned above.

To illustrate the methods employed in giving this training it will be necessary to give at the same time an account of the equipment which has been provided for this novel line of work.

As the term opens at the beginning of the school year one man out of the class is assigned as foreman of the chemical works and is given three or four of his classmates as assistants. In his assignment he is instructed to make an estimate for the manufacture of a certain chemical; to see that his machinery is put in perfect condition; to inspect his shafting, belts and motors; and to see that everything is in order, and that his factory is kept clean.

This being his first experience at handling men, he is watched very closely. The first chemical which is manufactured is usually barium chloride or a similar compound. Hence while he is having the plant put in working condition he details one of his crew to make an analysis of the witherite in order to determine the content of barium. This being ascertained he

makes his estimate as to the quantity of material necessary to produce any desired amount. He may then be told to estimate on four thousand pounds, it being understood that the weighings are to be made in grams (4000 grams). He includes in his estimate the market prices of raw material, freight f. o. b. New York, wear and tear of machinery, cost of labor and containers. Having decided that he can manufacture this product at a profit, he next puts his men to crushing and grinding the mineral, which is accomplished by means of a power-driven crusher, and grinder. The powdered mineral is then introduced into a porcelain-lined ten-gallon steam jacketed kettle where it is treated with the necessary amount of water and acid. In using the kettle in place of the evaporating dish he becomes acquainted with the method of heating by steam, and learns to regulate his pressure to secure the best results. Having precipitated the iron and other foreign matter, he passes the hot solution through a suction filter, which operation takes about five minutes for the contents of his kettle. This you will note is somewhat shorter and more satisfactory than the old time filter paper. The filtrate is immediately returned to the kettle or vacuum pan and run down to a gravity of about 65° Bé. As this density is reached the hot solution is transferred to crystallizing tanks and allowed to cool, the tanks used for this purpose being old alcohol barrels which have been sawed in the middle. When all of the salt has crystallized the mother liquor is returned to the kettle for further concentration while the crystals are dried in the centrifugal machine. Should the compound prove to be impure, it is again recrystallized, as only a C. P. product is accepted.

The remainder of the equipment in the chemical works consists of a vacuum still, vacuum pump, iron steam jacketed kettle, a porcelain-lined kettle with arbor, two filter presses, copper retort, condenser and large drying-oven. During the time which each student occupies in the factory he is given preparations which necessitate the use of all of the above machinery. As one gang finishes its assignment, another takes its place, continuing the work of the previous week and making new products as required. When all of the class have served a sufficient time in the chemical works, this factory is closed and the machinery cleaned and oiled.

Following the above line of work comes instructing in soap-making which is accomplished by means of a miniature soap factory, consisting of a lye tank, kettle, crutcher, frames, slabber, cutting machine, chipper, mill, plodder and press. The foremanship system is, of course, employed here, the one in charge being held responsible for the quality and quantity of the output. Here the student becomes familiar with the preparation of boiled, half-boiled and cold-made soaps, as well as the methods of slabbing, cutting, chipping, milling, perfuming, plodding and pressing. The size of our crutcher is sufficient for a one hundred pound charge, which when worked up into market form produces about eight hundred cakes.

Outside of the knowledge gained in the manufacture of soap this training gives self-confidence and the satisfaction of making something which is of practical use. During the past year we have made about twenty-five hundred pounds of toilet soap, which I am pleased to say has found a ready market.

The installation for the manufacture of pigments, paint, and varnish consists of three steam-heated precipitating tanks, three settling tanks, filter press, ball-mill, change can mixer, cone mill, kneading machine and varnish kettle. The object of this plant is to give instruction in the preparation of lakes and pigments, the grinding in oil, the manufacture of ready-mixed paints, the manufacture of oil stains, the boiling of oils and the preparation of varnish.

For instruction in the manufacture of leather the equipment consists of three pits 2 × 4 × 4 feet made of cypress and used for soaking, lining and for vegetable tannage. To demon-

strate the process of leaching a set of four vats 18 inches by 3½ feet are arranged in battery and steam-heated. Adjoining the tan-yard is a power-driven pin-mill, 3 feet in diameter by 13 inches wide, making 18 revolutions per minute. Next to the pin-mill is a paddle box 3½ feet long, 2½ feet wide by 2 feet deep, being driven at the rate of 40 revolutions per minute. A glass top slating table, beams, staking stand, slickers, knives, etc., are also provided, while in the roof of the building we have our drying-room, dust box and coloring table.

Thus it will be seen that the equipment lacks nothing for hand work. Splitting machines, shaving machines and such accessories are yet beyond our reach, but we have hopes that some day in the not far distant future these may also be added to our list. The skins as we receive them are in the dry salted or pickled condition and are put through all of the operations of soaking, lining, puering, tanning, scouring, shaving, retanning, dyeing and finishing, both mineral and vegetable tannage being employed.

As we have numerous excellent textile schools in this country we do not try to devote much time to the mechanical side of the industry. On the other hand we do give quite a bit of attention to the methods employed in the manufacture and use of dye-stuffs. Thus our organic preparation work is devoted almost exclusively to the manufacture of various coal tar product. For the practical application of these colors there is provided a reel, three two-gallon steam jacketed copper kettles, a steam-heated calcium chloride bath with opening for ten beakers, four dye vats, one jigger for piece goods and a printing machine. A kior is also installed for bleaching purposes.

To give an idea of the extent to which this practical work is conducted I will give a list of the materials manufactured by the students during the past year.

Chemicals (inorganic).....	500 lbs.
"    (organoic).....	80 "
Dye stuffs.....	20 "
Synthetic oils.....	5 "
Toilet soap.....	2500 "
Ready-mixed paint.....	50 gals.
Spirit varnish.....	10 "
Oil varnish.....	10 "
Oil stains.....	10 "
Worsted yarn (dyed).....	20 lbs.
Cotton yarn ".....	20 "
Silk ".....	8 "
Piece goods ".....	600 yards
Leather (tanned).....	240 skins

Whether or not this method of instruction will meet the requirements of the manufacturer remains yet to be seen. Undoubtedly changes will have to be made as we progress in the work. We feel confident, however, that it is a move in the right direction, and we hope for ultimate success.

PRATT INSTITUTE,  
BROOKLYN, N. Y.

## NOTES AND CORRESPONDENCE.

### THE DETERMINATION OF IRON AND ALUMINA IN INORGANIC PLANT CONSTITUENTS.

That the estimation of iron and alumina in the presence of phosphoric acid, manganese, calcium and magnesium is a somewhat troublesome operation is evidenced by the fact that the Association of Official Agricultural Chemists has adopted no method for the determination of these two elements in inorganic plant constituents.

The method which has been in use for some time in this laboratory has been found quite satisfactory; and, as it contains some modifications that we have not seen suggested as applicable to the analysis of ash, we have briefly outlined it below.

**Separation of the Iron and Alumina.**—To an aliquot of a solution of the ash corresponding to one gram add pure ferric chloride of known strength more than sufficient to combine with all phosphoric acid present. To the cold solution add concentrated solution of sodium carbonate until permanent precipitate just begins to form. Clear with 1 cc. of 80 per cent. acetic acid, add one gram of sodium acetate and boil for three or four minutes. When the precipitate has settled sufficiently to determine that the solution is colorless, filter at once before the precipitate becomes slimy. To insure the removal of all the lime from this precipitate it should be dissolved with hydrochloric acid into the same beaker, thereby preventing the necessity of washing beaker and precipitate. The iron and alumina are then reprecipitated with ammonia, filtered, dried, ignited, and weighed. The weight obtained, minus the  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  found by other methods and the known amount of  $\text{Fe}_2\text{O}_3$  added, will be the weight of the  $\text{Al}_2\text{O}_3$  in the ash.

In this method a great deal depends upon the proper adjustment of the sodium carbonate and the acetic acid. If too much sodium carbonate is used lime and magnesia may precipitate. Too much acetic acid may prevent the proper precipitation of iron and alumina.

The solution of ferric chloride which is added produces a red precipitate that is easier to filter and wash, makes a clearer filtrate and insures a complete precipitation of the phosphoric acid.

**Determination of Iron.**—To an aliquot of a solution of the ash determine iron by the Zimmermann-Reinhardt modification of the potassium permanganate method. Methods for determining iron in inorganic plant constituents by means of potassium permanganate have been offered before. The referee of the A. O. C.<sup>1</sup> recommended one modification of this as an official method of that association last year. All the methods, however, call for reduction of the iron by means of zinc, which necessitates the removal of the hydrochloric acid before the reduction can be proceeded with, and failures to remove all the hydrochloric acid, or to completely reduce the iron to the ferrous state are frequent sources of error when iron is determined in this manner. The danger of converting a part of the iron into an insoluble form when removing the hydrochloric acid by evaporation, and of not completely removing all zinc before proceeding with the titration are also frequent causes of error when this method is used. The Zimmermann-Reinhardt modification of the permanganate method in which the ferric iron is instantly reduced with stannous chloride, then titrated with the permanganate in the presence of the hydrochloric acid, after the addition of a "titrating" solution of manganese sulphate, phosphoric and sulphuric acid, is a decided improvement both in rapidity and accuracy over the use of zinc for reduction when iron is to be determined with potassium permanganate solution. R. F. HARE.

NEW MEXICO AGRICULTURAL COLLEGE.

## THE ADAMKIEWICZ-SENEX TEST FOR CASEIN IN PAPER.

The Adamkiewicz test for casein sizing in paper consists in extracting the paper with borax solution, precipitating the dissolved casein with acid, drying and warming gently with a mixture of two parts glacial acetic acid and one part concentrated sulphuric acid. The gradual development of a purple color indicates the presence of casein. This test has been simplified by Senex,<sup>2</sup> who moistens the paper with the reagent and warms slightly.

The simplicity of this test induced us to try it in this laboratory, and it was found that a casein-sized paper readily gave

the reaction; but unfortunately a check sample of paper sized with rosin also gave the purple color. This is not surprising in view of the similarity between the above mixture of acids and the acetic anhydride-dilute sulphuric acid (sp. gr. 1.530) mixture used in the Liebermann-Storch test for rosin. Further tests showed that powdered rosin, wood pulp and pine shavings, as well as casein, responded to this test. It is evident that before testing a sample of paper for casein it must be first thoroughly extracted with alcohol acidified with acetic acid in order to remove all rosin sizing that may be present.

C. E. WATERS AND J. C. BENEKER.

BUREAU OF STANDARDS.

## THE SEPARATION OF BISMUTH FROM ALLOYS CONTAINING ALSO LEAD AND TIN.

The separation of bismuth from the associated metals in fusible alloys presents some difficulties when working according to the more obvious methods.

An expedient which renders the estimation simple, has not come to the attention of the writer, and he therefore risks the following:

The acid filtrate from the mixed nitrates filtered from the tin oxide, is treated with a moderate excess of potassium or sodium hydroxide solution. This precipitates the bismuth and cadmium if present, and redissolves the lead hydroxide.

The oxides are filtered off, washed, and dissolved in hydrochloric acid. The bismuth is precipitated in the well-known manner as basic chloride, by being poured into a large quantity of water.

By getting rid of the lead in the manner indicated there is no complication resulting from the precipitation of basic salts of bismuth where they are not wanted. CHAS. E. SWETT.

## ON THE COMPOSITION OF LINSEED OIL FOOTS.

A few years ago G. W. Thompson published a very interesting article on the composition of the "break" from linseed oil.<sup>4</sup> He found that by heating a sample of linseed oil to about 400° F. he obtained 0.277 per cent. of a non-oilaceous substance which yielded 47.79 per cent. of ash consisting mainly of calcium and magnesium phosphates and less than 1 per cent. of nitrogen.

The authors had occasion to examine a sample of linseed oil "breaking-foots" which were obtained on a large scale from several thousand gals. of oil, the latter having been obtained by the naphtha extraction process. The oil had been heated to 500° F. through the direct introduction of superheated steam, and the foots were collected in a centrifugal machine. In this state the foots represented a brownish black dry mass of a consistency resembling that of soft cheese, and appeared free from oily matter. Extraction with carbon bisulphide showed, however, that 75.8 per cent. of the substance was still soluble in carbon bisulphide. The analysis of the soluble part proved it to be linseed oil, as shown by the following figures:

Specific gravity.....	0.9410 at 60° F.
Saponification value.....	191.3
Iodine value.....	160.6 per cent.
Hexabromides.....	8.2 per cent.
Acid value.....	5.3

The discrepancies between these values and those known for raw linseed oil are evidently due to the heating process to which the oil has been subjected.

The insoluble residue resembled in its appearance ground cocoanut shells and yielded the following analytical data:

<sup>1</sup> J. Am. Chem. Soc., 1903, page 1005.

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., Bull. 122, 93.

<sup>2</sup> Papierfabrikant, 1908, 395; Mitth. kgl. Materialprüfungsamt, 27, 153 (1909).



	Per cent.
Silica.....	0.23
Manganese oxide.....	1.00
Calcium oxide.....	23.53
Magnesium oxide.....	14.51
Phosphorus pentoxide.....	60.30
Sulphuric acid.....	none
Total.....	99.57

So far the results are a very close check to Thompson's work.

Another sample of foots which we subjected to an analysis represented settlings from the bottom of a tank containing raw linseed oil made by the extraction process. It was much more difficult to remove the oleaginous matter from these foots, but the appearance of the residue that proved insoluble in carbon bisulphide did not differ materially from the residue in the former case. The analysis of the extracted oil was as follows:

Saponification value.....	202.6
Acid value.....	14.5
Hexabromides.....	12.5 per cent.
Iodine value.....	145.3

Although these figures differ quite materially from those of raw oil, they point clearly to the fact that no other oleaginous matter but linseed oil was present in the foots. It will be remembered that the removal of the solvent at a comparative y high temperature and the small quantities on hand cannot fail but exercise a strongly oxidizing influence.

The insoluble part of these foots contained 0.57 per cent. nitrogen, and the ash analyzed as follows:

	Per cent.
Silica.....	12.53
Manganese oxide.....	0.51
Calcium oxide.....	3.17
Magnesium oxide.....	6.25
Phosphorus pentoxide.....	72.75
Total.....	85.21

The final filtrate showed a strong qualitative test for potassium.

The presence of silica in these foots is quite interesting, and was not observed in the foots obtained by the "breaking process."

Another sample of settling foots from raw oil obtained by the "naphtha process" showed a yet higher percentage of silica in its ash:

	Per cent.
Silica.....	34.38
Calcium oxide.....	7.98
Magnesium oxide.....	8.39
Phosphorus pentoxide.....	46.50
Potassium oxide.....	present

It was feared that the silica in this case might be due to mechanically suspended impurities of a sandy nature. In order to settle this question, the foots were dissolved in petrol ether and filtered through properly selected paper, whereupon the solvent was evaporated. The subsequent analysis was a very close check to that reported above which seems to prove that the silicious matter was a genuine constituent of the foots in question.

Contrary to this, a sample of settling foots from oil obtained by the hydraulic press system showed a total absence of silica:

	Per cent.
Silica.....	none
Calcium oxide.....	3.26
Magnesium oxide.....	4.99
Potassium oxide.....	10.27
Phosphorus pentoxide.....	81.08

All these samples show a tremendous preponderance of acid radicals over basic radicals.

OTTO EISENSCHIME,  
H. N. COPTHORNE.

AMERICAN LINSEED CO., SO. CHICAGO, ILL.

## BOOK REVIEWS AND NOTICES.

**Food Inspection and Analysis.** By ALBERT E. LEACH. Second Edition, Revised and Enlarged. Large 8vo., xviii, 954 pp., 120 figures, 40 full page plates. Cloth, \$7.50 net. New York: John Wiley & Sons.

When the first edition of Dr. Leach's book appeared five years ago it was eagerly seized and used by food chemists and inspectors and at once took a preeminent position among the works on the subject. It is seldom indeed that any book in its first edition shows such evidence of painstaking care in the preparation and in the selection and rejection of material. The first edition has now been thoroughly tried and in no sense has been found wanting. It is an excellent example of good authorship and good bookmaking.

The second edition is of the same high quality as the first. The pages have been increased from 787 to 954. New methods of analysis have been introduced, covering the following subjects: meat extracts, flour, noodles, paprika, prepared mustard, tea, coffee, cocoa products, ice-cream, maple products, honey, oils, distilled liquors and preservatives. There is a separate chapter on the various forms and applications of the refractometer and one on flavoring extracts, including those of almond, peppermint, wintergreen, rose, cassia and cloves.

The second edition of Dr. Leach's book will be welcomed by all chemists in the field of food inspection and analysis and will continue to occupy its important place for years to come.

W. D. RICHARDSON.

**Untersuchung der Mineralöle und Fette.** By DR. D. HOLDE.

Third Edition, 12 mo. Pp. xii + 459. Berlin: Julius Springer 1909. Price, 12 Marks.

The third edition of Dr. Holde's useful book contains several important modifications and additions. The chapters relating particularly to mechanical tests have been condensed, as have also other outdated matters and the analytical character of the book has been emphasized by utilizing the space thus obtained for extending the chapters: Specific Heat; Heat of Vaporization; Vaseline Lubricating Oil; Tar By-products; Turpentine, etc.

For a compact, concise book on mineral oils and fats, covering a large amount of ground, this work is unexcelled.

**Chemiker Kalendar, 1910.** By DR. RUDOLF BIEDERMANN.

Two Parts. Part I, xx + 50 + 385 pages. Part 2, 580 pages. Thirty-first year. Berlin: Julius Springer. 1910. Price, Cloth, 4 Marks; Leather, 4.50 Marks.

The Chemiker Kalendar, known to all, the chemist's *vade mecum*, now appears for the thirty-first consecutive year. It is probably true that Dr. Biedermann's work is possessed by more chemists and is more used from day to day than any other individual chemical book. It fully deserves its reputations because it is accurate, compact, comprehensive, well made and very moderate in price. For the current year nineteen pages have been added. As a suggestion to the author, the sulphuric acid tables of Lunge and Isler might well be supplemented by those of Ferguson and Talbot. Also the two parts might be combined and the whole bound in cloth or leather. Even so the book would be less bulky than many of the engineering handbooks.

**Iron Ores, Building Stones and Other Minerals.** WEST VIRGINIA GEOLOGICAL SURVEY. pp. 603, 24 page plates, 16 figures and maps. Post-paid, \$2.00; with maps, \$2.25.

This volume gives descriptions and analyses of all the principal iron ore deposits of the state, together with a history of the old charcoal furnace industry. The principal building stones of the state are also described and elaborate tests of their



strength and crushing limit made by the War Department of the Watertown Arsenal and also by the U. S. Geological Survey Testing Laboratory at St. Louis, together with chemical analyses, petrographic determinations, etc. The glass sands and salt industry are fully described and analyses given.

C. N. WILEY.

"The Utilization of Fuel in Locomotive Practice," is the subject of a bulletin just issued by the United States Geological Survey. The author, Professor W. F. M. Goss, of the Technologic Branch of the Survey, makes the statement that locomotives in service on the railroads of this country consume more than one-fifth of the total coal production of the United States:

Summary of results obtained from fuel burned in locomotives:

	Tons.
1. Consumed in starting fires, in moving the locomotive to its train, in backing trains into or out of sidings, in making good safety valve and leakage losses, and in keeping the locomotive hot while standing (estimated).....	18,000,000
2. Utilized, that is, represented by heat transmitted to water to be vaporized.....	41,040,000
3. Required to evaporate moisture contained by the coal.....	3,600,000
4. Lost through incomplete combustion of gases.....	720,000
5. Lost through heat of gases discharged from stack.....	10,080,000
6. Lost through cinders and sparks.....	8,640,000
7. Lost through unconsumed fuel in the ash.....	2,880,000
8. Lost through radiation, leakage of steam and water, etc.....	5,040,000
	90,000,000

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

Second annual meeting, December 8 to 10, 1909. Sessions held at Hotel Walton, Philadelphia, Pa.

#### PROGRAM.

WEDNESDAY, DECEMBER 8, 1909.

- 10.00 A.M.—Meeting at Hotel Walton.  
Address of Welcome, Mayor John E. Reyburn.  
Business Session.  
Reports of Officers and Council.  
Reports of Committees.
- 11.30 A.M.—Reading of Papers.  
(1) "Natural Draft Gas Producers and Gas Furnaces," Ernest Schmatolla. Discussion by O. K. Zwingenberger and G. E. Barton.  
(2) "The Commercial Extraction of Grease and Oils," W. M. Booth. Discussion by Frederick Dannherth, Louis Olney and Samuel P. Sadtler.
- 12.30 P.M.—Luncheon (Alternative). (Table d'Hôte 75 cents.)  
Luncheon was served at Hotel Walton for members who attended the excursion to the University and Commercial Museum.
- 1.30 P.M.—Excursions.  
Visit to Chemical, Engineering and Physical Laboratories of the University of Pennsylvania.  
Visit to Commercial Museum of Philadelphia, Dr. W. P. Wilson.
- 1.00 P.M.—Luncheon (Alternative).  
Luncheon was served by Harrison Bros. and Company, at their works for members holding admission cards for the excursion.
- 1.30 P.M.—Excursion.  
Excursion through the Chemical Works of Harrison Brothers

and Company, Thirty-fourth Street and Gray's Ferry Road. (Admission by card only.)

7.30 P.M.—Meeting at Hotel Walton.

Address of Retiring President, Dr. Samuel P. Sadtler.

Address, "The Chemical Industries of America," Prof. Chas. E. Munroe.

THURSDAY, DECEMBER 9TH.

9.30 A.M.—Excursions.

Members of Institute and their Guests will assemble at Race Street Wharf on the Delaware and be conveyed by the City Boat *S. H. Ashbridge* to the Torresdale Filtration Plant—returning stop at Tacony to visit the Wool De-greasing Plant of Erben, Harding and Company.

12.30 P.M.—Luncheon.

Luncheon at the works of Welsbach Light Company.

1.30 P.M.—Excursion.

Excursion through the works of the Welsbach Light Company.

3.00 P.M.—Excursion.

Return by boat to Kaighn's Point, Camden, and excursion through By-Product Coke Oven Plant of the Camden Coke Company.

5.00 P.M.—Return.

Return to Chestnut Street Wharf, Philadelphia.

7.00 P.M.—Dinner.

Subscription Dinner at the Hotel Walton (\$3.00).

FRIDAY, DECEMBER 10TH.

9.30 A.M.—Meeting at Hotel Walton.

Installation of Officers and Business Meeting.

10.30 A.M.—Reading of Papers.

(3) "Multiple Effect Distillation," F. J. Wood (Mechanical Engineer of Marx and Rawolle's Glycerine Refinery).

(4) "The Advantages of the Multiple Effect Distillation of Glycerine and Other Products," A. C. Langmuir. Discussion by P. B. Sadtler and Chas. L. Reese.

(5) "Reclaiming of Waste India Rubber," S. P. Sharples. Discussion by Wm. M. Grosvenor.

(6) "The Permanence and Acidity of Hydrogen Peroxide Solutions," Launcelot W. Andrews.

12.00—Luncheon at Hotel Walton (Table d'Hôte 75 cents).

1.00 P.M.—Excursion to Trenton.

Leave Broad Street Station for Trenton, N. J., at 1.00 P.M.

2.00 P.M.—Excursions.

Trenton Potteries.

The Hamilton Rubber Company.

Linoleum Works.

7.30 P.M.—Reading of Papers.

(7) "Materials for Textile Chemical Machines," Frederick Dannherth. Discussion by Louis A. Olney and J. M. Matthews.

(8) "A Method for Smelting Iron Ore in the Electric Furnace," Edward R. Taylor.

(9) "Chemical Composition of Illinois Coal," A. Bement.

(10) "Heat Efficiency of Smokeless Combustion, and Heat Absorbing Capacity of Boilers," A. Bement.

9.00 P.M.—Final Business Meeting.

SATURDAY, DECEMBER 11TH.

Visit to Cement Plant at Allentown, Pa.

The attendance at the meetings and excursions of the Institute at Philadelphia was very satisfactory. The dinner on Thursday evening was well attended and great enthusiasm shown both by members and guests in the importance of the work undertaken by the Institute, especially in maintaining a high standard for its membership.

The following officers were elected for the ensuing year:

President, Dr. Chas. F. McKenna, 50 Church St., New York;

First Vice-President, Dr. F. W. Frerichs, 3828 Westminster Pl.,

St. Louis, Mo.; *Second Vice-President*, Dr. Edward G. Acheson, Niagara Falls, N. Y.; *Third Vice-President*, Dr. Eugene Harnel, Ottawa, Ont., Can.; *Secretary*, Dr. John C. Olsen, Polytechnic Inst., Brooklyn, N. Y.; *Treasurer*, William M. Booth, Dillaye Bldg., Syracuse, N. Y.; *Auditor*, Henry S. Renaud, 159 Front St., New York; *Directors for one year*, Geo. B. Adamson, Easton, Pa.; David Watson, 111 South Mountain Ave., Montclair, N. J.; Dr. Edward Gudeman, Postal Telegraph Bldg., Chicago, Ill. *Directors for two years*, Ludwig Heuter, Berkeley, Cal.; Thorn Smith, Portland, Mich.; H. F. Brown, DuPont Bldg., Wilmington, Del.; *Directors for three years*, Dr. William M. Grosvenor, 1123 Broadway, New York; Richard K. Meade, Nazareth, Pa.; Dr. S. P. Sadtler, 29 South 10th St., Philadelphia, Pa.

## PHILADELPHIA MEETING.

## Abstracts of Papers.

## THE UTILIZATION OF WASTE INDIA RUBBER.

Abstract of paper by S. P. SHARPLES, S.B.

This paper gives a résumé of the various methods which have been employed in recovering the waste of rubber of commerce.

It calls particular attention to the processes which were employed by the late Nathaniel Chapman Mitchell in the Philadelphia Rubber Works. Mr. Mitchell was the first to make a commercial success in this country of methods for utilizing worn-out rubber articles, such as boots and shoes. This was largely due to the fact that he discovered that sulphuric acid of 15 to 25° B. could be employed to remove the fiber from these goods without injuring the rubber. The process was at once stolen and utilized all over the country until at the present time it is used in many works.

## OIL AND GREASE EXTRACTION.

By W. M. BOOTH.

The properties of the solvents which can be used for the extraction of oils are given. The solvent power and the cost of each is given. On this basis the cheapest solvent is found to be naphtha. The construction of building tanks and extraction apparatus is discussed. Methods of operation are also given. The methods in use for the recovery of grease from garbage tankage and other waste products is given. Drawings of extraction apparatus are given and also a number of tables and curves giving the properties of various fats and oils.

## ELECTRIC FURNACE FOR THE SMELTING OF IRON ORE.

Abstract of paper by EDWARD R. TAYLOR, Penn Yan, N. Y.

Having found the electric furnace for the manufacture of carbon bisulphide one of the easiest of operation and control, an attempt has been made to apply these principles to other manufactures. The saving of the use of movable electrodes by the use of broken conductive carbons which in an important sense fulfil the same office. This system is especially adapted to large operations.

Arrangements are made to reduce the natural conductivity by feeding charcoal in a practically unbroken column down the center of the furnace and between the electrodes. Such column is also directed outwards in the four quarters of the furnace around which and between which the ore with fluxes is fed, maintaining four columns of coarse ore—outside of which are maintained mantles of fine ore directed by means of the lining of the furnace to form a movable lining and absorbent for the radiant heat—which is returned to the furnace with such heated ore. This operation is facilitated by screws working in the outer and cooler part of the fine ore forcing the same

into the heated interior of the furnace above the electrodes where the reduction and fusion is completed, as fast as melted the reduced iron falling between the electrodes into the hearth of the furnace from which it is tapped out.

Arrangements are also made for the circulation of CO to extend the zone of ore reduction.

## HEAT EFFICIENCY OF SMOKELESS COMBUSTION AND HEAT ABSORBING CAPACITY OF BOILERS.

By A. BEMENT, Chicago, Ill.

This paper gives the result of tests carried out to ascertain the loss of heat due to incomplete combustion. The results are given in a table showing comparative heat balance of an ordinary water tube boiler in which the combustion was incomplete and an improved boiler arranged for the reception of a fire-brick tile furnace roof which made it necessary for the gases to travel to the rear of the boiler before coming in contact with the water tubes. By this arrangement, complete combustion was secured as shown by the absence of smoke. The loss of heat due to incomplete combustion in the ordinary boiler was found to be 9.3 per cent., while in the improved boiler there was no loss. The method of making the determinations and calculations is given in full.

In the second part of the paper, the causes governing the efficiency of a boiler are discussed. The results of the efficiency of three boilers. The first is a well-known water tube boiler in which the gases enter among the tubes at the rear and pass diagonally across the tubes to the exit. In the second boiler, a baffle was inserted among the tubes so that gases flowed twice the length of the tubes. In the third boiler, two baffles were inserted so that the gases flowed three times the length of the tubes. The fuel saving in the single baffle over the plain boiler was 8.68 per cent., while the saving in the double baffle was 20.68 per cent. Complete data with reference to the coal, temperature of gases, steam, draft, power developed, etc., are given.

## THE ADVANTAGES OF MULTIPLE EFFECT DISTILLATION AND ITS APPLICATION IN OTHER LINES.

By A. C. LANGMUIR.

The Wood Process of glycerine distillation marks one of the most important advances made in recent years in this line.

The patent rights have been acquired by Marx and Rawolle, New York, in whose plant the process is now in successful use on a large scale.

The fuel economy is marked, a considerable increase in output per still being obtained at a fuel consumption of less than half of that formerly used.

A set of six stills in series is successfully at work with no diminution of efficiency in the last still as compared with the first.

The chief advantages of the process, aside from the fuel economy, consist in the ease of working, uniformity of product with varying crudes and the scientific control possible at all times. The process is largely automatic, less labor and less skill in handling being required.

Only a small body of glycerine is present in the heaters, stills and connections, and the prolonged heating of large bodies of glycerine with resulting loss in the average still is avoided.

The spraying of the glycerine through the steam avoids the shooting and foaming often met with when distilling certain crudes in the still generally used.

The process is applicable in any distillation where steam is used and the product obtained has a boiling point higher than that of water such as the distillation of the heavier products

of coal tar and petroleum of aniline, essential oils and the fatty acids of the candle industry.

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#### MULTIPLE EFFECT DISTILLATION.

By F. J. WOOD.

The various steps leading up to the present development of the art of glycerine distillation are described with particular reference to the fuel economy. The consumption of coal per pound of glycerine output is greater now than with the earlier system, as it has been found more economical to save glycerine from decomposition by the use of a flow of steam in a vacuum which greatly lowers the boiling point.

In the multiple effect apparatus, a superior economy of fuel is obtained by using but one flow of steam to a number of stills and condensers, the stills being arranged in series in regard to the steam flow, that is the steam from the steam jet of the first still flows through a series of stills alternating with condensers, the condensers being maintained at a temperature that will condense glycerine out of the steam, but not the steam itself.

The glycerine is forced through heaters by means of centrifugal pumps. The heaters are connected with the boilers and supply the heat necessary for the vaporization of the glycerine.

From the heaters the hot glycerine is sprayed down through the steam.

The combined vapors of steam, and glycerine pass into boiling water condensers whose temperature is maintained at such a point by means of a pressure regulator, that the glycerine, but not the steam, is condensed. The glycerine in condensing gives up its latent heat of evaporation to the boiling water. The steam passes on to the next still in the series to take up its quota of glycerine. Finally, after the last of the series of stills is passed, the steam together with the volatile impurities are condensed as sweet water in a cold water condenser.

In order to maintain a uniform vacuum throughout the system, there must be a free flow of steam and glycerine vapor without obstructions. In this system instead of forcing the steam down through the body of glycerine, the glycerine is pumped up and sprayed down through the steam and no back pressure to the flow of steam results.

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#### CHEMICAL COMPOSITION OF ILLINOIS COAL.

By A. BEMENT, Chicago, Ill.

This paper gives the chemical composition and heating power of the coal obtained from seams throughout the state. It is a summary of a large number of analyses.

# THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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## EDITORIALS.

### THE CAMPAIGN OF 1910.

THE Division of Industrial Chemists and Chemical Engineers is on the march. With organized forces and well-considered plans it is moving toward a definite objective. Its lines of attack are many but they all converge.

The objective of the Division is a *larger usefulness on a higher plane of service* for all those engaged in the application of chemistry to industry. We recognize that the public esteem in which our profession is held, the rewards which it may offer and the satisfaction which it may bring are finally to be determined by the capacity for useful service demonstrated by its members and that there is no surer way of helping chemists than by developing opportunities for chemists to help others. To this end the work of the Division has been organized, toward this it will be directed throughout the year and for this your enrolment and assistance are solicited.

As a first step toward solidarity, a better acquaintance and readier cooperation, the Executive Committee has directed the Secretary<sup>1</sup> of the Division to prepare a descriptive list of its registered members which shall contain not only the names and addresses of these members but a brief statement of their scientific activities and industrial affiliations. Through

<sup>1</sup> F. E. Gallagher, 93 Broad St., Boston.

the various committees to which more extended reference is made elsewhere in this issue, a concerted effort will be directed toward bringing the great industrial and trade associations into touch and sympathy with the work of the Division. Our committees will cooperate with them in the definition of trade terms, the standardization of trade customs, the preparation of specifications, and the development of standard methods of technical analysis. The Committee on Research Problems has been constituted not only to initiate research and devise research methods in industrial chemistry, but to cooperate and advise with trade associations as to effective methods of attacking industrial problems of broad general interest to their members. The Committee on Publicity will endeavor in self-respecting ways and with due regard to the dignity of the profession to secure a wider recognition of the importance and practical value of the chemist's work. Something of what may be accomplished in this regard is indicated by the results secured at the Boston meeting where on behalf of the Society at large about 500,000 words a day were distributed to the press throughout the country. Finally as affording direct help to our own membership and to chemists everywhere as well, reference should be made to the work of the Committee on Descriptive Bibliographies and to that of the Committee on Prices of Elements and Special Compounds. It is expected that a report of progress will be had from each of these committees at the San Francisco meeting.

A systematic effort has further been inaugurated to arrange with each of the large industrial associations for the attendance of a delegate at the meetings of the Division who shall transmit to his association all matters of interest to its membership. Ultimately it is hoped to secure reciprocal representation by the attendance of duly authorized members of the Division at these association meetings.

Such as the Division may hope to accomplish as an organization along the lines indicated and others equally beneficial in their reaction upon its membership and the profession as a whole, it remains true that the real uplift for a larger usefulness upon a higher plane of service must come from the sustained and daily effort of each one of us as individual representatives of our profession.

A. D. LITTLE.

### ORGANIZATION.

THE Boston meeting of the American Chemical Society, with more than 500 enthusiastic chemists



registered, is one more testimonial to the efficacy of wise scientific organization. The policies developed during the last four years of the Society's history are working out even better than the most sanguine advocate anticipated. Of those policies the organization of Divisions and the publication of special journals devoted to particular branches of chemistry are the most prominent and important, although the earlier organization of Local Sections and the creation of corporation membership must not be overlooked. There are several independent chemical organizations and independent chemical journals of a scientific type in America which have not yet joined issues with the American Chemical Society. It is unnecessary to state that these societies and publications are doing excellent work. Nevertheless the thought must arise again and again in the mind of an unprejudiced observer as to the possibilities, if complete organization of the chemical forces in America could be brought about.

### THE DISTILLATION OF WHISKEY.<sup>1</sup>

By A. B. ADAMS, CHEMIST, BUREAU OF INTERNAL REVENUE.

Received November 17, 1909.

Until recently but little attention has been paid to the chemistry of whiskey, and practically none to the changes taking place in its distillation. As to what occurred in the different parts of the process, what was the composition of the different portions of the distillate and residues, but little was actually known. The work of Schidrowitz<sup>2</sup> has been about the only work published on this part of the subject, and as this is upon the methods as used in the British Isles, where the processes of making whiskey differ somewhat from those used in this country, it was thought desirable to obtain some data upon the processes used in this country. It is with the view of shedding some additional light on the subject that this paper is offered.

In the United States nearly every distiller uses one of two kinds of stills for the first distillation. The three-chambered beer still, either wooden or copper, is used in Maryland and Pennsylvania; in Tennessee and Kentucky the small ten- or twelve-chambered continuous beer still is used. It was, therefore, decided to obtain samples representative of a day's run from a distillery in Pennsylvania using the three-chambered beer still, and one in Kentucky using the continuous beer still.

The Pennsylvania distillery selected, uses a three-chamber charge wooden beer still: the vapor pipe passes out of the center of the top of the still, then downward into the bottom of the doubler—a copper cylinder

about 30 inches in diameter, and as high as the beer still. Into this doubler are placed at the beginning of each charge the combined heads and tails of the previous charge. The vapors from the beer still enter this liquid, boil it, and pass out at the top of the doubler in a vapor pipe connected to a worm where they are condensed.

The object of cutting out and returning the heads and tails to the doubler appears to be to cut out of the whiskey those portions of the distillate which contain undesirable products, such as an excess of aldehydes, and certain indeterminate bodies occurring in the tail of the run, called by many fusel oil, which, however, are proven by these analyses not to be "fusel oil" or the higher alcohols. By reboiling, the alcohol is saved and the "undesirables" gradually disappear, partly by chemical change and partly by elimination.

Starting with the still in operation and a charge just run—it being charged every 28 minutes—the slop or spent beer in the lowest chamber is drawn off, and the partly dealcoholized beer in the second chamber dropped into the bottom chamber; the contents of the first or top chamber are dropped into the second chamber, and new beer (about 1,000 gallons) from the charging tank is emptied into the first chamber. The residue from the doubler of the beer still is emptied into the second chamber of the still, and the doubler recharged with the "heads" and "tails" of the previous run of the beer still, consisting of about 172 wine gallons, the composition of which can be seen by averaging the heads and tails in the proper proportion.

	Grams per 100 liters						Quantities, gallons.
	Proof.	Acids.	Esters.	Higher alcohols.	Aldehydes.	Ferments.	
Average of heads	111.4	7.2	126.7	83.0	166.18	0.90	12
Average of tails	61.2	9.6	15.8	3.0	7.0	0.4	166
Average	64.6	9.4	23.8	40.0	17.9	0.38	172 total
Contents of doubler at end of charge	27.6	0	6.1	trace	0.0	1.2	about

Live steam is then turned into the bottom chamber, a pressure of about 4–5 pounds being used. In about eight minutes the distillate begins to come over. The first runnings called "heads" are very turbid and are collected in the "low wine" tank as soon as the distillate clears, which takes about two minutes; a sufficient quantity is considered cut out as "heads;" the distillate is then turned into what is called the "high wine" tank, the contents of which are redistilled the following day. This "high wine," or "middle run," is continued for about five minutes or until the proof has dropped to 112 when the flow is again turned into the "low wine" tank where it is mingled with the "heads." The distillation is discontinued when a certain number of inches of low wines has been run and the proof has reached about 8°. The contents of the lowest chamber are now exhausted of alcohol

<sup>1</sup> Prepared in connection with the Commission of Internal Revenue. Read at the summer meeting of the American Chemical Society, Detroit, Mich., 1909.

<sup>2</sup> See Schidrowitz in *Royal Commission on Whiskey*, Vol. 1, Great Britain. Schidrowitz in *The Journal of the Institute of Brewing*, 1906.

and are drawn off. This is one cycle of the beer still and is repeated eighteen times each full day. By this method of operation the beer is finally separated into only two products, slop and "high wines," the "heads" and "tails" being again distilled in the next run of the still.

Four hundred bushels of grain are mashed in the proportion of forty-five gallons of water to the bushel, producing 18,000 gallons of beer each day. The "high wines" are collected from each of the eighteen charges forming one day's production, thoroughly mixed, reduced to 100° proof and the next day redistilled in a pot still, which is a large copper still about 8 ft. in diameter, 6 ft. high with a small dome, or boiling head, about 2½ ft. in diameter on top. The vapor pipe, about 7 inches in diameter, rising from this dome to a height of 15 ft., runs horizontally for about 15 ft. then down about 15 ft. to the worm. There is no return pipe of any kind on this still which would carry back any of the condensed vapors. The still holds 1900 wine gallons, and a closed steam coil or scroll is the source of heat.

The distillate in this case, as in the primary distillation, is separated into "heads," "middle run" and "tails." It takes about thirty minutes to run the "heads," about five hours for the "middle run," and one and a quarter hours for the "tails." The "heads" and "tails" are sent to the beer well in equal proportions for each 1000 gallons of beer in order that they may be redistilled in the beer still with the beer and keep the "middle run" free of off products. The "middle run" is reduced to proof and the succeeding day is bonded as whiskey. In this distillation as in the first, there is no final separation except into the "middle run," which is the finished product of the

still, and the "lees water" which is emptied into the sewer (the "heads" and "tails" being mixed with the beer).

On February 2, 1908, samples were taken as follows:

21699	Unfermented mash.....	Represents 18,000 gals.	
21700	Beer ready to be distilled.....	" "	
21701	Slop or spent beer as emptied from lowest chamber of beer still.....	" "	
<i>Beer still:</i>			
21702	Sample aver. of heads.....	Quantity, 12 gals.	Time of running, 2 minutes.
21703	1st of middle run.....	80 "	5 "
21704	middle of middle run.....		
21705	end of middle run.....		
21706	aver. of tails.....	160 "	12 "
21708	contents of high wine doubler at end of charge.....	172	
21709	aver. high wines of day.....	1900 gals.	at proof.
<i>Redistillation still:</i>			
21691	Sample as distillation started.....	40 gals.	30 minutes.
21692	of heads just before cutting off.....		
21693	middle run immediately after heads cut off.....	1200 "	5 hours.
21694	2nd middle run, 2 hours after 21693.....		
21695	3rd middle run, 1½ hours after 21694.....		
21696	4th middle run, 1½ hours after 21695.....		
21697	just as soon as tails started tails just before cutting off tails.....	250 "	1½ hours.
21698	lees or residue in still.....	400 "	
21707	An average sample of the middle run or whiskey before being diluted to proof.....		
21711	An average sample of the previous day's run diluted to proof.....		

The methods used were those in Bulletin 107 revised, Bureau of Chemistry, using the Allen Marquardt method for "fusel oil." The "fusel oil" on "slops" and "lees" was determined by saponifying 500 cc. and distilling as usual.

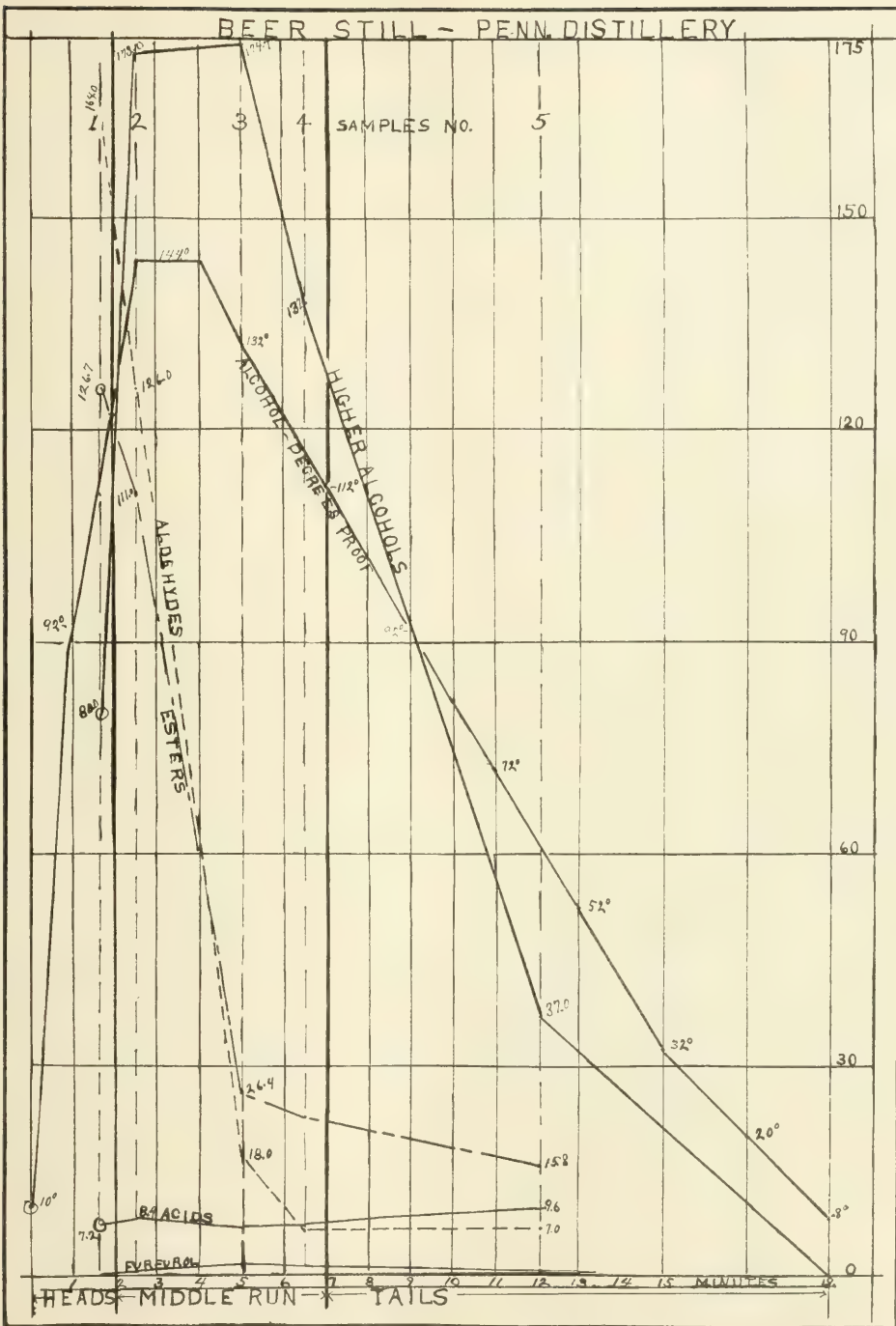
The analysis of these samples is as follows:

		Grams per 100 liters.				
	Proof.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Higher alcohols.
21699 Unfermented mash.....	0.0	93.6		trace	0.0	2.0
21700 Beer ready for distillation.....	10.4	381.6		"	0.0	19.1
21701 Slop or exhausted beer.....	0.6	290.4		"	0.0	2.6
<i>Beer still:</i>						
21702 Heads—average of one charge.....	111.4	7.2	126.7	164.0	0.0	80.0
21703 1st sample from middle run.....	144.3	8.4	110.9	126.0	1.4	173.0
21704 2nd sample from middle run.....	133.6	7.2	26.4	18.0	2.6	174.7
21705 3rd sample from middle run.....	117.3	7.2	22.9	7.0	2.4	137.3
21706 Tails, average of one charge.....	61.2	9.6	18.8	7.0	0.4	37.0
21709 Average of high wines or singlings, day's production.....	138.3	4.8	38.7	36.0	1.6	170.0
<i>Redistillation still:</i>						
21691 1st heads, very first run.....	94.1	2.0	95.0	78.0	0.0	50.0
21692 2nd heads, just before heads cut off, ½ hour later.....	163.2	2.4	70.4	94.0	0.80	160.0
21693 Middle run immediately after heads cut off.....	163.7	4.8	56.3	96.0	0.85	160.4
21694 2nd middle run, 2 hours after 21693.....	157.5	6.0	18.8	"	1.55	265.4
21695 3rd middle run, 1½ hours after 21694.....	153.4	4.8	7.0	2.1	1.7	349.4
21696 4th middle run, 1½ hours after 21695.....	114.7	3.0	14.1	1.5	6.0	153.6
21697 Tails immediately after middle run cut off.....	95.2	4.2	15.8	1.2	7.5	74.4
21698 Tails just before finishing of tails.....	15.4	3.6	8.8	0.0	2.6	10.2
21707 Lees water.....		2.4	8.8	trace	0.0	2.0
21710 Finished product before dilution.....	150.0	3.0	21.1	14.9	1.55	288.2
21711 Finished product after diluting for bonding (product of previous day).....	100.9	1.2	18.8	6.5	1.0	191.9

NOTE.—When the acids were first determined the results in some of the cases were higher than is here reported, due, it was found, to the presence of CO<sub>2</sub>. Also, wherever aldehydes were present in excess, the higher alcohol content was increased, the aldehydes, therefore, had to be destroyed by means of metaphenylenediamine hydrochloride.



# BEER STILL - PENN. DISTILLERY





the "heads," 17.3 per cent. in the "tails" (these are afterwards redistilled in the beer), and 64.0 per cent. in the finished product, leaving to be eliminated in the lees water 17.2 per cent.

*Esters.*—On consulting the curves we see that in both the beer still and the second distillation, the first runnings contain the largest proportion of esters, but rather quickly drop to a normal amount throughout the remainder of the distillation. Of the esters that are found in the distillates from the second still, 10 per cent. are eliminated in the lees, and about 18 per cent. found in the "heads" and "tails," leaving 72 per cent. in the finished goods. But the total quantity of esters found in these portions is only 66 per cent. of the amount in the "high wine singlings" of the day, showing apparently that some 34 per cent. of esters are lost or changed during the redistillation.

*Aldehydes.*—Careful work on the mash, beer and "slop" failed to show more than a trace of aldehydes, and yet in the distillate there is a very appreciable amount, indicating that they are formed during distillation. The curve of the beer still results show that aldehydes are present in large proportions in the "heads," the curve then dropping rather quickly to a minimum amount which is maintained throughout the run. The "slop" is entirely exhausted of aldehydes. The results prove a separation in the "heads" of 33 per cent., in the "tails" 19 per cent., and in the "slop" nothing but a trace (indeterminable), leaving in the "high wines," to be redistilled, a total of 48 per cent. of the aldehydes distilled, which consists of the aldehydes present in the previous "heads" and "tails" and those formed during distillation.

In the redistillation, the aldehydes, after the first runnings, almost immediately attain their highest point in the curve, the major portion being distilled within two and one-half hours after the still is started; the curve gradually drops to a minimum until the last sample of the "tails" is reached where the results show no aldehyde. A calculation of the amounts in the different fractions proves that in the "heads" there are separated 16.0 per cent., in the "tails" 0.7 per cent., and in the "lees" none, leaving in the finished product 83.3 per cent. of the aldehydes which are in the sum of the different fractions of the redistillation.

As has been said, the beer ready for distillation contained but a trace of aldehydes but of course a trace of aldehydes in 18,000 gallons of beer would amount to something in the high-proof "spirits" distilled from it. On calculating the total of aldehydes present in the "high wine" back to the beer, we find that we should have a content of 2.7 parts per 100,000, whereas we actually have a trace. The aldehydes in the "high wine" represent also, the

aldehydes which were in the "heads" and "tails" of the previous redistillation, but this figures to 0.2 part per 100,000, leaving still a total of 2.5 parts in the beer, or produced during distillation, but, as has been shown, it is not in the beer, therefore, it must be formed during the distillation of the beer by the oxidation of the alcohol.

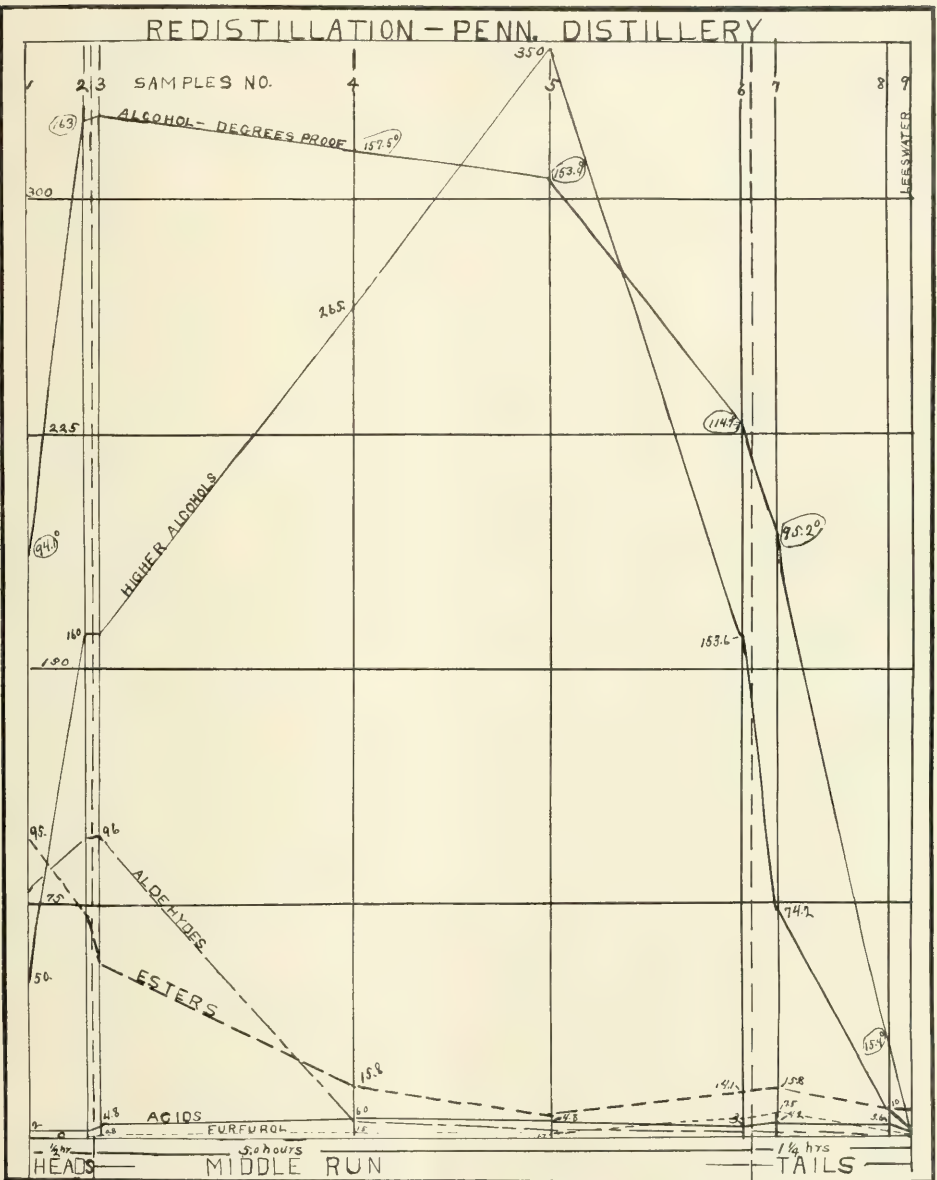
Comparing the amounts in the "high wine" and in the finished product, recognizing, of course, that they represent different days' goods, we find that there was in the "high wine" 0.4940 of a gallon, and in the redistillation products 0.2147, a loss of 56 per cent. in the process of redistillation. One would therefore conclude that during the distillation of the beer by means of live steam, aldehydes are formed by oxidation; during the redistillation, which is conducted by means of a steam coil, aldehydes are lost, which is probably caused by further oxidation into acids.

*Furfurols.*—In the examination of the mash, beer and "slop," I was unable to obtain even the faintest reaction for furfural. The results of the beer still expressed in a curve start from nothing in the "heads," increasing gradually to the highest point at the middle of the distillation; it then drops slowly to nothing at the end of the run. There is then no separation of furfural in the "heads," about 35 per cent. in the "tails" (which are returned to the doubler), and none in the "slop," leaving in the high-wine run 65 per cent. of the furfurols produced.

In the redistillation the curve is very similar with the exception that the highest point is not reached until the running of the "tails" or until 70 per cent. of the contents have been distilled. The results show a separation of 0.79 per cent. in the "heads," 6.3 per cent. in the "tails," and absolutely none in the "lees water," leaving in the finished product 92.9 per cent. of the furfurols which are present in the products of the second distillation, or 89 per cent. of the furfurols present in the "high wines" are found in the finished product, proving that there is practically no change in the furfural content by redistillation, and further, that all the furfural produced is found in the finished product. These results seem to prove that furfural is produced at this distillery during the distillation of the beer, probably through the action of the live steam.

The Kentucky distillery, whose product was next examined, uses a continuous copper beer still, containing fourteen chambers. The still is about four feet in diameter and twenty feet in height, heated by live steam. This type of still differs from the charge chamber still in that, in the latter, the contents of each chamber are let down into the next lower chamber by the beer runner at the end of each charge period. While in the continuous still, as the name implies, there is no interruption to the process, the beer is pumped in at the top of the still (heated nearly to the

# REDISTILLATION - PENN. DISTILLERY



boiling point) in a continuous stream, flows through the down pipe into the next plate or chamber, flows across this plate (which is perforated with holes through which live steam is continually ascending)

the "tails." The "tails" are mixed with the beer to be distilled the next day; the "backings" are emptied into the sewer.

The following are the results of analysis:

Grams per 100 liters.					
	Proof.	Acids as acetic.	Esters as acetic	Aldehydes as acetic	Furfural. Higher alcohols.
1 Beer from tub No. 9.....	...	54.0	..	0.54	0.05
2 Beer from tub No. 9.....	...	54.6	..	0.74	trace
3 Slops from 1st distillations.....	...	39.3	..	0.36	trace
<i>Beer still:</i>					
4 Singlings taken at 11.07 A.M.....	71.7	21.0	42.4	1.0	0.0
5 Singlings taken at 11.30 A.M.....	67.7	20.4	49.3	0.9	0.0
6 Singlings taken at 11.53 A.M.....	71.7	21.0	45.8	0.8	0.0
<i>Redistillation still:</i>					
7 Foreshots taken at 12.27 P.M.....	40.5	16.2	73.9	10.3	0.0
8 Spirits taken at 12.29 P.M.....	153.2	6.0	95.0	16.3	0.0
9 Spirits taken at 12.55 P.M.....	139.0	5.4	38.7	1.4	0.0
10 Spirits taken at 1.25 P.M.....	46.0	18.0	36.9	0.0	0.0
11 Average sample—bonded.....	102.1	6.6	40.6	2.6	0.0
12 Tails taken at 1.30 P.M.....	33.4	18.0	38.7	0.0	0.0
13 Tails taken at 1.33 P.M.....	24.4	19.2	40.5	0.0	0.0
14 Tails taken at 1.38 P.M.....	17.1	20.4	33.4	0.0	0.0
15 Backings.....	0.0	43.2	17.6	0.0	0.0

to the opposite side where it flows over into the down pipe of the next chamber, and so on until the bottom of still is reached and the beer is completely dealcoholized. No "heads" and "tails" are cut out because the flow of spirit is uniform in quality.

The singlings are redistilled in a horizontal pot still shaped very similar to a steam boiler with a dome about 12 ft. in height, and 3 ft. wide, the vapors passing out of the top of the dome, through a small vapor pipe, then into the worm. There is no return pipe on this still.

The following samples were taken on March 8, 1909.

1 Beer from tub No. 9, representing.....	8370 gallons.
2 Beer from tub No. 9 (duplicate)	
3 Slop or exhausted beer, representing.....	9300 gallons.
<i>Beer still:</i>	
4 Singlings taken at 11.07 A.M.	
5 Singlings taken at 11.30 A.M., representing.....	1236 gallons.
6 Singlings taken at 11.53 A.M.	
<i>Redistillation still:</i>	
7 Foreshots taken at 12.27 P.M.	
8 Spirits taken at 12.29 P.M.	
9 Spirits taken at 12.55 P.M.	
10 Spirits taken at 1.25 P.M.	
11 Average (of 7-10) of whiskey as bonded.....	875 gallons.
12 Tails taken at 1.30 P.M.	
13 Tails taken at 1.33 P.M.....	175 gallons.
14 Tails taken at 1.38 P.M.	
15 Backings or "leeswater".....	361 gallons.

The samples above described are representative of the distillation of the same beer, that is, the beer in tub No. 9 was followed from the beer well to the bonding room. The "singlings" began to flow at 10.45 A.M. and ceased at 12.12 P.M.; therefore, the "singlings" samples are representative of the entire run, as this still produces "spirits" of the same proof from the beginning to the end of the run. (It was impracticable to obtain a sample of the "singlings" after they had been mixed.)

The redistillation started at 12.26 P.M.; the first sample was taken one minute after the flow started, and the second sample three minutes after. Sample No. 10 was taken just before the flow was turned into

The acids of the beer are rather low, there is a determinable amount of aldehydes and a trace of furfural. The analysis of the samples from the continuous beer still proves what might be expected, that the distillate of a continuous beer still has the same composition at any and all parts of the run, each of the three samples containing practically the same percentages of both alcohol and congeneric products.

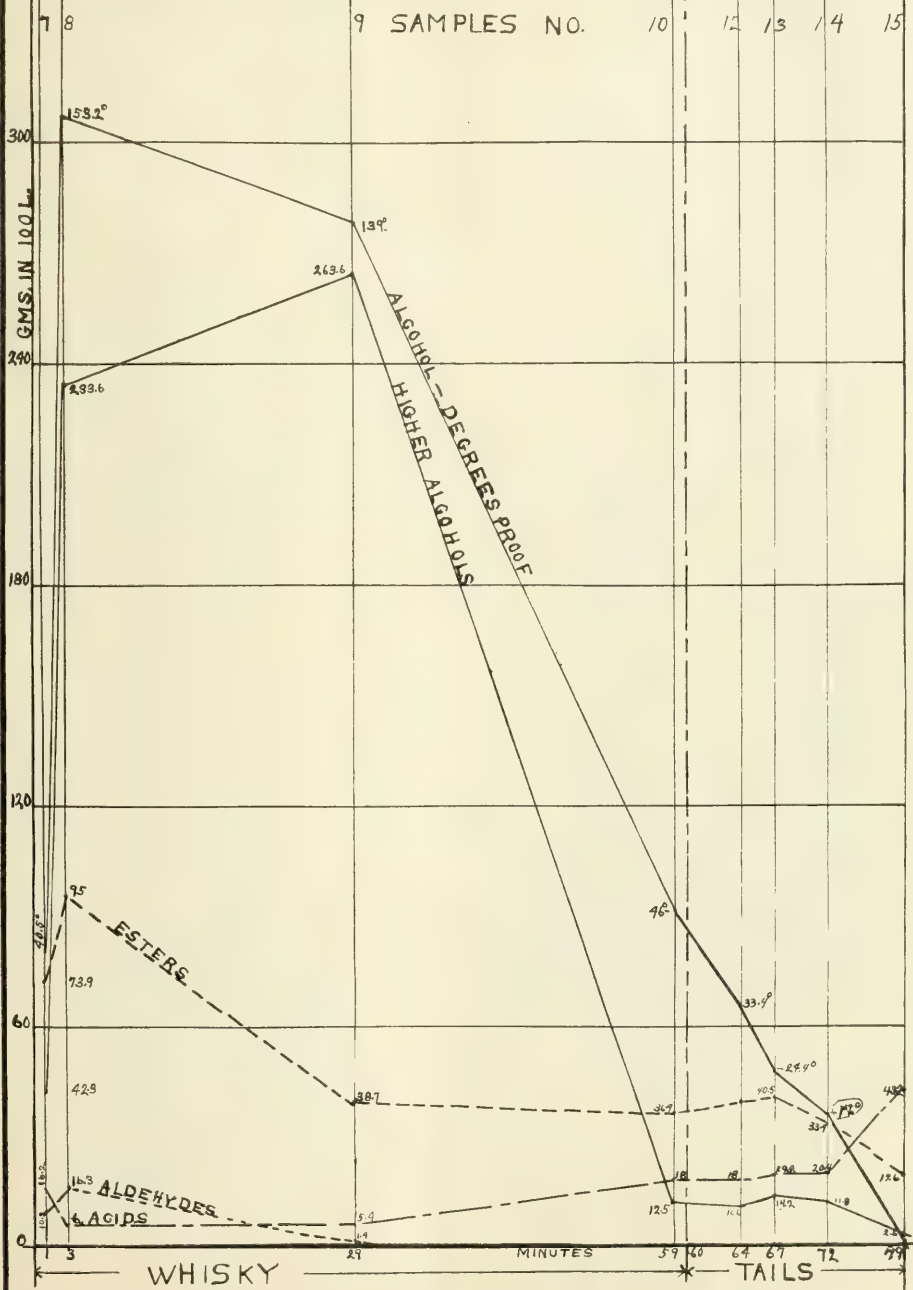
On comparing the difference in the beer and "slop," and that found in the "singlings," we find that only a small per cent. of the acids distilled appear as such in the distillate.

It is noticed that but a minimum of aldehydes appear in the first distillate, the continuous still evidently tending to decrease the content of this ingredient. The beer and "slop" gave an affirmative reaction for furfural, which is reported as a trace. The singlings do not show even a trace of furfural, proving that the continuous still does not produce furfural during the course of the distillation of the beer, as evidently the three-chambered still does. (This conclusion has been checked by the analysis of the product of at least seven different distilleries using a continuous beer still.) The examination of the slop for the higher alcohols shows only a trace; therefore, practically all of the higher alcohols produced during fermentation are distilled, and appear in the "singlings" to be afterward redistilled.

*Redistillation.*—In the redistillation we find that the "heads" or "foreshots" are not separated at this distillery but form part of the finished product. (This policy is followed at many houses on account of the fact that much of the flavoring matter seems to be present in the first runnings of the distillation.) The "spirits" are distilled much faster here than in the Pennsylvania distillery. The same remarks made upon the previous redistillation apply here; the proof starts low for reasons previously given, but in two



# REDISTILLATION - KENTUCKY DISTILLERY



minutes runs true, and the curve is then a straight descending line.

The acids drop gradually, starting at 16.2, but at the last sample of the "middle run" increase, leaving in the "backings" a higher proportionate acidity (acetic) than was present in the "singlings." The per cent. of acids eliminated in the "backings" is about 63 per cent. of the total acidity of the "singlings."

**Esters.**—The esters distil as in the other redistillation with the exception that the curve is more nearly horizontal, due, probably, to the more speedy distillation. Reducing the proportion of esters to a comparable basis we find that there are present in the "singlings" 0.5661 gallon,

In the whiskey	0 3553 gallon,
In the "tails"	0 0656 "
Backings	0 0634 "
	0 4843 "

or in the whiskey, 73.4 per cent. in the "tails," 13.5 per cent. in the "backings," 13.1 per cent. of the esters resulting from the redistillation. This amount is only 85.5 per cent. of the esters in the "singlings," a loss of nearly 15 per cent. during redistillation.

**Aldehydes.**—The examination for aldehydes proves the greatest amount to come over in the first few minutes of the distillation, while all has come over before the end of the whiskey or "middle run." There are no aldehydes in the "tails," and none in the "backings." There is about twice as much aldehyde in the whiskey as in the "singlings," this is directly opposite to that which occurred in the other distillery.

**Furfurals.** There was no furfural in the "singlings," and there is none in the redistillation (but furfural is found after this whiskey has been in a charred barrel).

**Higher Alcohols.**—The results are the same as in the other redistillation, a very small amount appears in the "backings." A calculation of the higher alcohols shows 1.253 gallons in the "singlings," 1.4131 in the whiskey, 0.0214 in the "tails" and 0.0094 in the "backings," showing slightly more higher alcohol in the redistillation product than in the "singlings."

#### RECAPITULATION

Pennsylvania Distillery.— <i>Singlings.</i>				
Heads.	Middle run.	Tails.	Slop or lees.	
Per cent.	Per cent.	Per cent.	Per cent.	
4.4	60.4	28.9	Trace	Higher alcohols.
3.8	27.3	68.9	..	Acids.
21.3	43.3	35.4	..	Esters.
33.0	43.3	18.7	..	Aldehydes
0.0	65.0	35.0	..	Furfural.
Pennsylvania Distillery.— <i>Redistillation.</i>				
1.2	95.6	3.0	0.2	Higher alcohols.
1.5	64.0	17.3	17.2	Acids.
9.4	71.9	8.7	10.0	Esters.
16.0	83.3	0.7	...	Aldehydes.
0.8	92.9	6.3	...	Furfural.

#### Kentucky Distillery.—*Singlings.*

No separation to heads and tails.

#### Kentucky Distillery.—*Redistillation*

No heads.	Whiskey or middle run.	Tails.	Backings.	
Per cent.	Per cent.	Per cent.	Per cent.	
...	97.8	1.5	0.7	Higher alcohols.
...	23.4	13.6	63.0	Acids.
...	73.4	13.5	13.1	Esters.
...	100.0	..	..	Aldehydes.
...	...	..	..	Furfural.

This is probably due to errors of the method increased by the multiplication necessary for this calculation. In per cents. 0.07 are eliminated in the backings, and 1.5 per cent. pass over into the "tails" and are redistilled next day, proving that 99 per cent. of the higher alcohols produced are in the finished product.

In conclusion, I would state that, in my opinion, the following facts are proven regarding the changes occurring during the distillation of whiskey as practiced in this country.

(1) Practically all of the higher alcohols (or "fusel oil") are found in the finished product, only slight traces being eliminated in the spent beer and lees-water. This statement applies to both the charge chambered beer still and the continuous beer still.

(2) That certain chemical changes occur:

a. In the acids, as is proven by the difference between the amount eliminated from the beer and the amount found in the finished product, the finished product being almost neutral, yet no appreciable quantity of acids is found in the "lees," except at the Kentucky distillery.

b. In the esters, as is proven by the loss in redistillation.

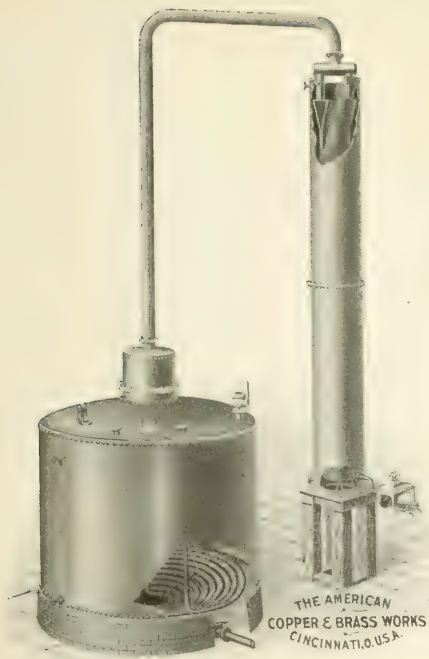
c. In the aldehydes, as is proven by the loss in redistillation at the Pennsylvania distillery. If there were no chemical changes, the still would finally become completely choked with aldehydes. This does not occur, as the content of aldehydes runs fairly consistent throughout the season.

(3) That furfural is a product of distillation in a three-chambered beer still, or a still operating on this principle, and is not a product of the continuous beer still.

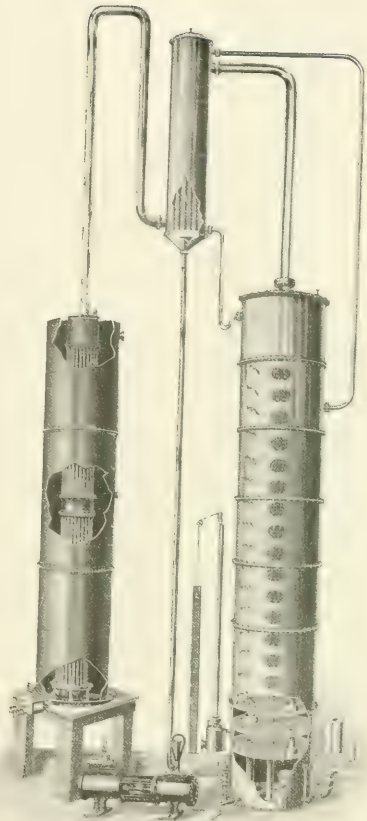
(4) That the substances which produce the unpleasant odors, frequently found in the "tail" of the distillation and in the "lees," are not "fusel oil" as is commonly supposed, but factors at present indeterminate, probably being water-soluble products of fermentation distilled over from the beer.

Credit should be given to Messrs. A. W. Schorger and Peter Valaerr for able assistance in the analytical work.

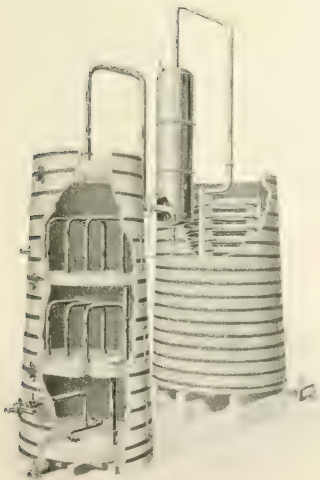
I desire to express my thanks to the American Copper and Brass Works, of Cincinnati, Ohio, for the loan of the illustrations of the stills.



Redistillation still.



Continuous beer still.



Three-chambered charge beer still.





## THE DETECTION OF FISH OILS IN VEGETABLE OILS.

By OTTO EISENSCHIML AND H. N. COPTHORNE.

Received December 17, 1909.

The present methods for the positive detection of fish oils in linseed oil are extremely unsatisfactory. The analytical propensities of drying oils on one hand and most fish oils on the other are indeed so similar that the commonly used quantitative reactions are not applicable, and that an estimation of the proportions in a given mixture of some of them practically defies our present state of knowledge.

The similarity of linseed oil and menhaden oil in particular is very aggravating, and as a mixture of these is well within the realm of practical problems, the experiments described later were carried out with the object of developing a qualitative test for the positive identification of menhaden oil in linseed oil.

So far as the authors know, the methods used at present in cases of this kind may be divided into the following groups:

- (1) Color tests.
- (2) Tests founded on the different properties of the ether-insoluble bromides of the fatty acids.
- (3) The phytosteryl acetate test.

Of these tests the color tests are entirely unreliable, while the others named require more or less skill and time for their proper execution. It was deemed advisable, therefore, to develop methods by means of which fish oils and vegetable oils can readily be differentiated.

It is very strange that oils of such different origin as linseed oil and menhaden oil should show such remarkable parallelism, not only in regard to their physical and chemical constants but also in regard to other properties.

Hehner and Mitchell have called attention to the peculiar fact that pure linseed oil soap imparts an odor to the cleaned fabric which strongly resembles that of fish oil. It is also remarkable that if linseed oil is heated to about 500° F. for a short time or to a lower temperature for a greater length of time it will assume a fish-like odor, a fact which is leading to numerous and unjustified complaints from consumers of pure boiled linseed oil.

The first experiments carried out were based on the assumption that fish oils may contain nitrogenous organic compounds of alkaline character. This fact in itself is easy of verification but could not be made the basis of a qualitative test.

It was next proposed to make use of the observation that the drying of linseed oil and menhaden oil proceed in a different manner, and that, therefore, the amount of oxygen absorbed in a given length of time might prove useful for further work along these lines. It was soon demonstrated, however, that the differences observed were not sharp enough; besides,

fish oils of supposedly the same origin varied considerably in this respect.

A variation of this method consisted in the extraction of fine silica which had been saturated with the oils in question, and exposed to heat for the purpose of oxidation. It was hoped that after a certain length of time the amount of fish oil that could be extracted by means of solvents would be considerably higher than that in the case of linseed oil. This was indeed the case, as out of parallel samples the percentages of oil extracted would be for instance, 21.8 per cent. in case of linseed oil, and 77.0 per cent. in case of fish oil. Nevertheless, this line of research had to be abandoned, as the results obtained were by no means definite enough.

While it is a well-known fact that the physical and chemical constants of linseed oil and menhaden oil are almost identical, very few data could be found that would allow a comparison between these two oils after an oxidizing treatment. In order to obtain the figures desired, we subjected both linseed oil and menhaden oil to processes of heating and air-blowing, and the products of oxidation and polymerization which resulted in parallel cases were analyzed with the hope of finding some striking discrepancies. Unfortunately, it developed that the specific gravities, saponification numbers, iodine values, hexabromides, and other characteristics changed in both oils in apparently identical manner. Although the results were negative as bearing on the point in question, some interesting data were obtained which will be published at some other time.

It was finally decided to return to the insoluble bromine compounds as giving the best promise of success. By brominating fish oils and linseed oil, respectively, in various solvents, it was discovered that the compounds formed differed considerably in solubility, as shown below.

	Linseed oil bromides.	Menhaden oil bromides.
Chloroform.....	Soluble.	Insoluble.
Petroleum ether.....	Insoluble.	"
Benzole.....	Slightly soluble.	Slightly soluble.
Carbon bisulphide.....	Soluble.	"
Carbon tetrachloride.....	Slightly soluble.	"

This suggests at once the following qualitative differentiation: If a few drops of linseed oil are dissolved in chloroform and bromine is slowly added in the cold, no precipitate will form, while menhaden oil produces a distinct cloudiness.

It is indeed possible to discover the presence of menhaden oil in linseed oil by means of this method, but unfortunately, it was impossible to filter the apparent precipitate. If the cloudiness was all that could be determined, the test would class with color tests and other reactions of the purely subjective nature, while if the precipitate formed could be weighed, a distinct advantage was to be gained. We

endeavored to accomplish this by means of a special filtering medium prepared of burnt magnesia and asbestos fiber, but without result. Admixtures of inert matter like Fuller's earth, the use of a centrifugal machine, the heating of the cloudy solvent for weeks with the aid of a condenser, and other means remained likewise without result. We were, therefore, compelled to abandon chloroform as a medium for the process of bromination, and the next experiment undertaken was to determine whether the amount of insoluble bromides from solvents other than ether would lead to useful conclusions. The results obtained were very disappointing, and the filtration of such precipitates as were obtained proved, as a rule, highly unsatisfactory.

The substitution of iodine for bromine gave no useful results.

If equal parts of chloroform and glacial acetic acid are used to dissolve linseed oil and menhaden oil, and bromine is added to the respective solutions, a cloudiness develops in either case. If, however, both liquids are heated to the boiling point of water, the apparent precipitate dissolves in the case of linseed oil, while in the case of menhaden oil a sandy precipitate settles on the bottom of the vessel. It was soon found that this reaction gave very sharp and uniform results, and would prove the basis for a useful test. A great number of substances were examined in this manner with the following results:

PRECIPITATE SOLUBLE ON HEATING.

Linseed oil.	Olive oil.
Chinese wood oil.	Castor oil.
Cottonseed oil.	Cocanut oil.
Corn oil.	Rosin.
Peanut oil.	Rosin oil.
Rape seed oil.	Tar oil.
Mustard seed oil.	Paraffine oil.

PRECIPITATE INSOLUBLE ON HEATING.<sup>1</sup>

Crude menhaden oil.
Light pressed menhaden oil.
Dark pressed menhaden oil.
Bleached winter menhaden oil.
Winter white menhaden oil.
Bleached winter whale oil.
Bleached winter seal oil.
Domestic cod liver oil.
Newfoundland cod liver oil.
Norwegian cod liver oil.
Tanners' cod liver oil.
Medicinal cod liver oil.
Dogfish oil.
Herring oil.

A qualitative test on this basis is carried out as follows: 100 drops of oil are dissolved in 6 cc. of a mixture containing equal parts of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown coloration remains. After 10 or 15 minutes the test tubes are placed in a beaker containing boiling water. Linseed oil and other vegetable oils will clear up completely within a few seconds, while fish oils will remain cloudy and precipitate an insoluble bromide at the bottom of the tube within

a short while. It is easy to detect 10 per cent. of fish oil in vegetable oils by this method, and with very little practice even 5 per cent. of fish oil are clearly recognizable.

In case of boiled linseed oil it is necessary to remove the metallic constituents before adding the bromine. This is preferably done by shaking with a 10 per cent. solution of nitric acid saturated with potassium nitrate. If both the oil and the acid are warmed up previous to the shaking in the funnel, the separation will be almost immediate. In order to remove any traces of moisture from the oil, it is suggested to filter the same through a double layer of paper.

The accuracy of the test made it appear probable that the reaction might be turned into a quantitative method. About 1 gram of the oil was dissolved in 10 cc. of chloroform and 10 cc. of glacial acetic acid. The bromides were formed and left standing for three hours. Some difficulty was experienced in filtering the precipitate hot through a Gooch crucible, but a little improvised apparatus soon permitted us to surround the crucible with a jacket of boiling water. The precipitate was then washed with equal parts of hot chloroform and hot glacial acetic acid, and finally dried on a water bath.

A sample of manhaden oil examined in this manner furnished 9.1 per cent. insoluble bromides, and it was easy to check this result very closely several times. The same menhaden oil was then mixed with raw linseed oil in various proportions, the insoluble bromides were filtered out, and the amount of menhaden oil figured on the basis of 0.0 per cent. for linseed oil, and 9.1 per cent. for menhaden oil. The results obtained are embodied in the following table:

Menhaden oil present.	Menhaden oil found.
Per cent.	Per cent.
10.6	9.1
20.5	21.2
16.1	17.0
19.6	20.5
19.6	18.9
27.8	27.9
21.4	21.5
16.6	15.7

The bromides insoluble in hot chloroform and glacial acetic acid (1 : 1) were then determined for various fish oils with the results as given below.

	Per cent	
Crude menhaden oil.....	9.1	1st sample.
Crude menhaden oil.....	23.0	2nd sample.
Bleached winter menhaden oil.....	17.8	
Winter menhaden oil.....	14.7	
Light pressed menhaden oil.....	15.0	
Tanners' cod liver oil.....	9.6	
Norwegian cod liver oil.....	9.5	1st sample.
Norwegian cod liver oil.....	11.7	2nd sample.
Domestic cod liver oil.....	15.2	1st sample.
Domestic cod liver oil.....	14.2	2nd sample.
Medicinal cod liver oil.....	15.5	

These results show that it will not be possible to use this method for quantitative analysis unless a minimum figure of fish oil present is all that would be

<sup>1</sup> The substances are given here by the names under which they were obtained from wholesale houses.



desired. It seems that the amount of insoluble bromides in oils of the same kind but from different sources varies to a considerable extent.<sup>1</sup>

It is on account of heating and other oxidizing processes to which the oil are subjected before they reach the market that no real quantitative method will ever be worked out on the lines laid out above. The fact, however, that the precipitate formed can be weighed, and is indeed in direct proportion to the amount of fish oil present in a given sample, elevates this reaction above the level of an ordinary qualitative test, and therein lies a very important advantage over the methods now in use. The short time required for the performance of the test and its applicability to both raw and boiled linseed oil are other factors of importance.

#### CONCLUSIONS.

The following test for fish oils of any kind in admixtures with vegetable oils or similar products is suggested. 100 drops of oil are dissolved in 3 cc. of chloroform and 3 cc. of glacial acetic acid. Bromine is added slowly, and after about 10 minutes the test tubes are placed in boiling water. All vegetable oils clear up, while fish oils remain cloudy. By filtering and weighing the precipitate formed, it is possible to obtain objective results.

In case of boiled oils it is necessary to remove the metallic salts before adding the bromine.

Fish oils that have been heated to 260° C. or more for some time will not respond to this test.

The authors desire to express their gratitude to Miss Gertrude Stock who performed a large proportion of the analytical work carried out in connection with the above investigations.

LABORATORY OF AM. LINSEED CO.,  
SO. CHICAGO, ILL.

### THE DETERMINATION OF PHOSPHORUS RETAINED WITH FERRIC CHLORIDE IN THE ETHER SEPARATION.<sup>2</sup>

By R. J. WYSOR.

Received December 23, 1909.

The use of ether as a medium for effecting the separation of iron from other metals in oxidized

<sup>1</sup> In corroboration of our results we quote from a private communication of L. M. Tolman, of July 7, 1909.

<sup>2</sup> "I must say, however, that my experience with these fish oils is such as would make it seem almost impossible to make any standard on their composition, the various determinations showing such a tremendous variation on oils of absolutely known origin. This wide variance you will note in connection with the iodine absorption of the cod liver oils themselves, and also the amount of bromine precipitate formed."

<sup>3</sup> "In connection with this matter, we must state that we found it impossible to obtain samples of absolutely known origin through the Bureau of Fisheries at Washington. In reply to our request for fish oil samples of known origin, H. M. Smith, Acting Commissioner of the Bureau of Fisheries at Washington, stated that he had no samples of oil on hand, and was not in a position to procure them for us. Referring to our remarks that commercial fish oils vary considerably in their constants, and that market samples probably had been oxidized, Mr. Smith wrote that "menhaden oil is subjected to heat when the fish are cooked, and also after the oil is pressed out, and in the process of refining."

<sup>4</sup> Read at the December meeting of the Pittsburg Section, American Chemical Society.

hydrochloric acid solutions has long had practical application in analytical chemistry. J. W. Rothe, in his original paper on this subject,<sup>1</sup> discusses in detail his experiments and the method by which the ether separation is accomplished. Carnot, in a later publication,<sup>2</sup> pursues an investigation along the same general lines as Rothe, and adds one or two metals to the list of those which may be separated from the bulk of iron by the ether method. Recently, Andrew A. Blair<sup>3</sup> has shown that molybdenum, in common with iron, exhibits an affinity for ether, and that a complete separation of this element may thus be effected from the other metals.

The writer has discovered no literature which treats of the behavior of phosphorus, or other non-metallic elements, in company with iron in the ether separation. In reviewing Rothe's article, the statement was found that no attempt had been made to determine whether ferric phosphate, or ferric sulphate could be separated from acid solutions.

It is the purpose of this paper to consider the behavior of relatively small amounts of phosphorus in the ether separation, under somewhat empirical conditions, in order that a certain critical value may be attached to the discussion. Conditions of experiment commonly occurring in practice were chosen, thus affording a commentary upon an existing application of the ether method, to which reference will subsequently be made.

In a number of preliminary experiments, a steel of very low phosphorus content was employed, together with a standard phosphorus solution, prepared by dissolving diammonium hydrogen phosphate in hydrochloric acid (1.13 sp. gr.). A sufficient volume of this solution to represent the amount of phosphorus desired was added to 1, 2 or 3 grams of the steel. A further addition of enough hydrochloric acid (1.13 sp. gr.) to make a total volume of 40 cc. was then made, and after solution had been effected, the ether separation was made in the same manner as later described. Although interesting results were obtained, comparable with those secured in the ensuing work, their practical value was not evident, and the following materials were selected as the basis of experiment.

Two iron ores were chosen of the same soluble iron content, 57.5 per cent., and of widely variant soluble phosphorus content, 0.060 per cent. and 0.510 per cent. These ores were mixed in such proportions as to represent approximately even gram weights of metallic iron, and definite weights of phosphorus as subsequently noted.

An iron ore of 68.6 per cent. soluble iron content

<sup>1</sup> *Mittheilungen aus den Königlich Tech. Versuchsanstalten zu Berlin*. 1892, Part III.

<sup>2</sup> "Méthodes d'Analyse des Fontes, des Fers, et des Aciers," 1895, p. 123, et seq.

<sup>3</sup> *Journal American Chemical Society*, 1908, p. 1229.

and 0.050 per cent. soluble phosphorus content was used in conjunction with a standard phosphorus solution. This solution was prepared by dissolving diammonium hydrogen phosphate in dilute hydrochloric acid, and was carefully standardized so that each cubic centimeter contained 0.0005 gram of phosphorus.

Several other iron ores were subjected to sufficient experiment to indicate that approximately the same results were obtainable as those described in this paper.

*Method of Procedure.*—The requisite weight of the single ore, or of the two ores to represent 1, 2 or 3 grams of metallic iron, was employed. In the latter case, the respective ores were properly proportioned to yield 0.001, 0.002, 0.004, 0.008 or 0.016 gram of phosphorus as desired in the mixture. In the treatment of the single ore, the proper volume of the standard phosphorus solution was added, which together with the phosphorus content of the ore would afford the desired weight of this element. All calculations were based on the soluble iron and phosphorus content of the ores as previously mentioned. The numerical results obtained by these analogous procedures appear in the appended tables in parallel columns.

The calculated weight of the single or mixed ores was digested in strong hydrochloric acid, with the aid of a gentle heat, for two hours, or until no further solvent action was apparent. The solution was diluted and filtered, the residue, after being washed free of iron discoloration, being discarded. If the standard phosphorus solution was to be added, the addition was made at this point, and the filtrate evaporated to dryness. The residue was dissolved in 40 cc. of hydrochloric acid (1.13 sp. gr.), gentle heat being applied to aid solution. The solution was cooled in water, and transferred to a single-chambered, cylindrical-shaped, separatory funnel, provided with a ground glass stopper, and having a capacity of about 175 cc.

Anhydrous ether (distilled over sodium) was used for all the separations, 40 cc. being employed for 1 gram of iron, 75 cc. for 2 grams and 100 cc. for 3 grams. Part of the measured amount of ether was used to rinse the dish, from which the solution had been transferred, the rinsings with the remainder of the ether being transferred to the separatory funnel. After thorough agitation under cold, running water, the solutions were allowed to stand several minutes to permit as complete a separation as possible. The lower stratum was then carefully drawn off and discarded. The ethereal solution, containing the bulk of ferric chloride, if not subjected to further treatment, was washed with a sufficient quantity of water to remove all the iron and concomitant phosphorus.

A second series of determinations was made in the same manner as just described, except that after the

lower, acid solution had been drawn off, the ether solution was rewashed with 10 cc. of ether-saturated hydrochloric acid (1.13 sp. gr.). The solutions were again allowed to stand several minutes, the lower stratum was drawn off and discarded, and the ether solution washed with water as previously described.

The final solution, containing nearly all the iron, with the residual amount of phosphorus to be determined, was warmed to volatilize the remaining ether, then the excess hydrochloric acid expelled by evaporation. The determination of the phosphorus was completed by the well-known gravimetric method.<sup>1</sup>

The interesting behavior of phosphorus under the varying conditions of experiment may readily be interpreted from the tabulated results, and the accompanying diagrammatic presentation.

TABLE I PERCENTAGE OF PHOSPHORUS RETAINED IN THE ETHEREAL SOLUTIONS OF IRON.

Total phosphorus present. Gram.	Mixed ores. Percentage of total phosphorus retained with 1 gram iron.	Total phosphorus present. Gram.	Ore plus standard phosphorus solution. Percentage of total phosphorus retained with 1 gram iron.
0.00104	23.2	0.001	24.0
0.002	19.0	0.002	18.7
0.004	18.3	0.004	17.0
0.008	17.5	0.008	15.9
0.016	16.9	0.016	15.8
2 grams iron.			2 grams iron.
0.00208	33.0	0.00146	32.3
0.004	32.3	0.002	31.3
0.008	30.6	0.004	30.9
0.016	29.7	0.008	29.5
3 grams iron.			3 grams iron.
0.004	35.2	0.00219	37.7
0.008	34.8	0.004	35.1
0.016	35.4	0.008	35.5
		0.016	35.9

TABLE II PERCENTAGE OF PHOSPHORUS RETAINED IN THE ETHEREAL SOLUTIONS OF IRON, REWASHED WITH 10 CC. OF ETHEREALIZED HCl (1.13 SP. GR.).

Total phosphorus present. Gram.	Mixed ores. Percentage of total phosphorus retained with 1 gram iron.	Total phosphorus present. Gram.	Ore plus standard phosphorus solution. Percentage of total phosphorus retained with 1 gram iron.
0.00104	22.3	0.001	22.0
0.002	15.8	0.002	15.4
0.004	13.4	0.004	12.7
0.008	12.3	0.008	12.2
0.016	11.6	0.016	12.2
2 grams iron.			2 grams iron.
0.00208	24.7	0.00146	26.2
0.004	24.2	0.002	24.6
0.008	23.5	0.004	23.4
0.016	23.3	0.008	22.8
3 grams iron.			3 grams iron.
0.004	28.0	0.00219	26.8
0.008	26.0	0.004	26.6
0.016	26.5	0.008	25.2
		0.016	26.1

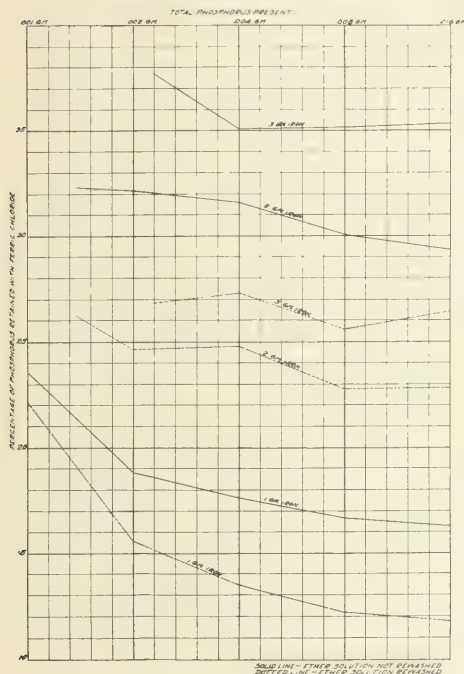
From the preceding results it is evident that under fixed conditions, a fairly constant percentage of the phosphorus present remains with the iron, in the ether separation. This phenomenon at once suggested a

<sup>1</sup> Described in the methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Iron Ores.

practical adaptation of the results obtained. In methods for the estimation of alumina, involving an ether separation of the iron, followed by an ammonia precipitation, it has been assumed that all the phosphorus present remained with the alumina and the other metals. In the ether method for the determination of alumina, as described in the methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Iron Ores, a correction is

DIAGRAM OF THE  
PERCENTAGE OF PHOSPHORUS RETAINED  
IN THE ETHER SOLUTIONS OF FERRIC CHLORIDE

DERIVED FROM THE AVERAGE RESULTS FOR CORRESPONDING AMOUNTS  
OF PHOSPHORUS IN THE MIXED OXIDES OF IRON AND ALUMINA AND FROM  
THE STANDARD PHOSPHORUS SOLUTION



applied to the weight of the mixed oxides of iron, aluminum and phosphorus by deducting the combined weights of iron (determined by titration) as ferric oxide, and the total phosphorus content of the ore as pentoxide. The conditions of experiment represented in Table I of this paper are practically the same as those existing in the above-mentioned method. The approximate error incident to this method may, therefore, be calculated and the proper correction applied.

For convenience in reference, Table III, appearing below, has been prepared for weights of phosphorus pentoxide and metallic iron; these conditions, of course, are to be observed in effecting the proper corrections. This table has been constructed from the

average of the corresponding results presented in the preceding tables. The figures here tabulated are additive values, to be applied as direct increments to the weight of the mixed oxides of aluminum, iron and phosphorus, previously noted. It will be seen that there is an increasing amount of phosphorus lost in the ether solutions with an increase of both the phosphorus and iron content of the ores, though the percentage error in the present ether alumina method is reduced by the use of large samples. Although corrective estimates are not given for intermediate variations of phosphorus and iron content, it seems rational to assume that they may be approximated by interpolation.

TABLE III.  
(Calculated from Table I.)  
Weight phosphorus pentoxide to be added  
to weight of alumina residue found.

Weight soluble phosphorus pentoxide in ore. Gram.	1 gram iron. Gram.	2 grams iron. Gram.	3 grams iron. Gram.
0.0023	0.0005	.....	.....
0.0046	0.0009	0.0015	0.0017
0.0092	0.0016	0.0029	0.0032
0.0183	0.0031	0.0055	0.0064
0.0366	0.0060	0.0108	0.0130

(Calculated from Table II.)

0.0023	0.0005	.....	.....
0.0046	0.0007	0.0011	0.0012
0.0092	0.0012	0.0022	0.0024
0.0183	0.0022	0.0042	0.0047
0.0366	0.0044	0.0084	0.0097

In order to determine the behavior of increased amounts of phosphorus in the ether separation, several experiments were performed according to the conditions of the second series of determinations, with weights of phosphorus ranging upwards to 1 gram, a strong standard solution being prepared for this purpose. The results obtained indicate that about the same percentage of phosphorus remains in the ether solutions with the presence of relatively greater amounts, as with the largest weight (0.016 gram) of phosphorus previously employed. Expressed diagrammatically, the lines representing the percentage of phosphorus remaining with the ferric chloride in the ethereal solutions, if prolonged, would suffer no further, appreciable depression.

LABORATORY OF DUQUESNE STEEL WORKS.

## THE INFLUENCE OF THE METHOD OF HEATING ON THE NON-VOLATILE ETHER EX- TRACT OF SPICES.

By ARTHUR LOWENSTEIN AND WILLIAM P. DUNNE.

Received January 6, 1910.

In a paper recently reported by us on "Spanish Paprika" we called attention to the fact that in heating the non-volatile ether extract of this spice to constant weight, the method of heating was an important factor. The official method of the A. O. A. C. calls for "heating to constant weight at 110° C.," without specifying how this is to be accomplished, and we take it that it is usually interpreted to mean



in an air oven. There are such a variety of types of air ovens—some constructed to secure circulation of air and others to prevent circulation—that the degree of change in heating in air ovens is a variable. That chemical change is involved in such a method of drying in the case of spices must be at once evident to the chemist, when he considers the nature of the extractives from spices, which in many cases consist of drying oils or glycerides of high iodine values, and of resinous and mucilaginous material. Extractives of such a nature when exposed in thin films to the action of the air at 110°C. naturally absorb oxygen and undergo change, and it is the object of this paper to show briefly the degree of change in certain cases. It must also be evident that such changes are not only confined to the extractives from spices; but also to other complex organic materials such as foodstuffs, particularly where the extract contains a drying or semi-drying oil as in the case of linseed or cottonseed meal.

In the present paper we have used the determination of the iodine number of the non-volatile ether extract of the spices to indicate the degree of change in such extract when heated to constant weight in an air oven as compared with the iodine number of the same extract heated *in vacuo*. Heating in an atmosphere of some inert gas might be advantageous, but is not quite so convenient as the use of a vacuum oven.

The ether extract was obtained by the regular A. O. A. C. method of continuous extraction for twenty-four hours with anhydrous, alcohol-free ether. We found it convenient to employ a quantity of the spice which would yield approximately 0.5 gram of extract. Duplicate extracts were heated in an air oven to constant weight after removal of the volatile ether extract in the usual way, and duplicates in each case were brought to constant weight in a vacuum oven at a temperature of 90°C. The period of heating was in the former case on an average about three hours. In the latter constant weight was always

secured in an hour and a half. It will be noted from the table that there is as a rule but little difference in the per cent. of non-volatile extract obtained in the two methods of heating, which would indicate that changes, other than simply oxidation, take place in the composition of the extract. Such changes are particularly noticeable in the color of the extracts. In certain species of capsicum, the color of the extract is completely discharged, and in other spices considerably altered, when heated in air, whereas there is usually but little if any visible change in the coloring matter when heated *in vacuo*. Changes in the solubility of the extract in organic solvents also occur when the heating has been conducted in air. This is particularly noticeable in the case of some spices when an attempt is made to dissolve the extract in chloroform prior to determining the iodine absorption number. In some cases a very considerable amount of the extract has been rendered insoluble, when heated in air. Such conditions have not been noted when heating in vacuum was employed. Marked changes in the consistency of the extract have been noted, which would be revealed by determinations of the melting point. Naturally other of the so-called "constants" would be similarly affected. The non-volatile ether extract was in each determination dissolved in chloroform, made up to a definite volume, and iodine numbers made on aliquot portions by the Hanus method.

In conclusion it might be stated that the ether extract of spices should be handled as quickly as possible, both in the determination of the volatile extract and in removing the volatile, air being excluded wherever possible, both in the oven and in desiccators, and if the iodine value is determined this should be done quickly after obtaining the non-volatile extract.

A glance at the table reveals quite wide differences in the iodine values of spices. It would appear that

Lab. No.	Description	Heated to constant wgt. in air oven. Temperature 110°C.		Heated to constant wgt. in vacuum oven. Temp. 90°C. Pressure 10 cm. Hg.		Difference in iodine numbers.
		Non-vol. ether extract. Per cent.	Iodine number.	Non-vol. ether extract. Per cent.	Iodine number.	
45277	Whole white pepper	(a) 6.75 (b) 6.69	{ 64.3 64.5 63.3 63.3	{ 6.87 6.80	{ 69.9 70.0 70.2 70.2	6.30
45278	Whole black pepper	(a) 8.66 (b) 8.66	{ 61.6 61.6 60.4 60.4	{ 8.10 8.25	{ 65.9 65.9 65.2 65.3	4.50
45279	Ground cayenne pepper sample No. 1.	14.50	{ 97.4 97.5	14.84	{ 122.2 122.2	24.8
45280	Ground cayenne pepper sample No. 2.	15.70	{ 92.9 92.9	16.60	{ 116.2 116.2	23.3
45281	Whole mace	(a) 29.73 (b) 29.48	{ 98.2 98.2 94.7 94.5	(a) 29.30 (b) 29.20	{ 99.6 99.6 100.5 100.6	5.2
45282	Shells from Mexican Chili pods	19.08	{ 106.2 106.2	19.0	{ 116.6 116.6	10.4



with such a simple method at hand this determination could be developed into one of considerable value in the detection of adulteration of spices.

That which precedes not only applies to the ether extract of spices, but to the ether extract of all complex organic materials. In fact it also applies to the determination of moisture in such materials, as somewhat similar changes take place when they are dried in air. In the determination of moisture the changes may frequently be greater, because the period of drying is in most cases longer.

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## REVIEWS.

### THE TEMPERATURE WORK OF THE BUREAU OF STANDARDS.<sup>1</sup>

By C. W. Waidner.

Received October 4, 1909.

In view of the interest manifested in the work of the Bureau of Standards by many of the members of the American Chemical Society, I have reviewed the work of the laboratories devoted to thermometry, pyrometry and heat measurements.

In the organization of the work much time was necessarily devoted to the establishment of standards, which would enable us to accurately define and reproduce a standard scale of temperatures throughout the widest range of measurable temperatures from that of solid hydrogen to that of the electric arc. Various liquid air comparators, electrically heated comparison baths, furnaces, etc., had to be designed and constructed, as well as much necessary apparatus, such as platinum resistance thermometers, special bridges to be used with them, calorimetric apparatus, etc. Much of this apparatus as well as the most varied kinds of temperature measuring instruments had to be carefully standardized and investigated for all possible sources of error. Much of this preliminary work, which from its very nature can never be regarded as completed, has been done, so that the Bureau is now in a position to standardize almost any type of instrument used for the measurement of temperatures from that of liquid air to that of the electric arc. The necessary plant is now available and as soon as time permits the lower range will be extended to the temperature of solidification of hydrogen.

The scope of the testing work now being done can, perhaps, be best made clear by the following illustrations from our annual report: thermocouples of various kinds used in the range  $-100^{\circ}$  to  $+1600^{\circ}$  C.; resistance thermometers used in scientific and industrial work in the range from  $-200^{\circ}$  to  $+1200^{\circ}$  C., some of these of special construction to measure the mean temperature of a large space, others to measure the temperature "at a point;" all of the leading types of optical and radiation pyrometers for temperatures from about  $700^{\circ}$  C. to the highest temperatures met with in electric furnaces; some ten to twelve thousand thermometers annually, including clinical thermometers used by physicians, alcohol and pentane thermometers for the measurement of low temperatures, the latter being available for temperatures as low as that of liquid air ( $-190^{\circ}$  C.), ordinary laboratory and primary standard thermometers for use in the range  $-35^{\circ}$  to  $550^{\circ}$  C., calorimetric and Beckmann thermometers for use in freezing and boiling point and in calorimetric investigations and principally

in the determination of the heating value of fuels, maximum and minimum thermometers, thread thermometers used to determine the mean temperature of the stem emergent from the bath and thus the necessary correction to apply to the observed reading of the thermometer, a correction which may exceed  $25^{\circ}$  in some cases; the determination of the specific heats and the heats of combustion of substances; standardized heat samples used in the standardization of combustion calorimeters; the viscosities, flash points and setting points of oils; the melting points of metals, alloys and ceramics; fire tests of materials; the temperatures of lamp filaments; the temperatures of an incandescent platinum wire for various heating currents; the critical points of steel and other alloys; etc.

As to the policy of the Bureau in accepting tests, it may be said that such tests as the standardization of thermometers, pyrometers, calorimeters, the determination of melting points etc., that cannot very well, be done by private laboratories, are made for the general public. Other tests, such as those relating to oils, the heating values of fuels, etc., which can very well be taken care of by private laboratories, are only accepted by the Bureau in special cases involving disagreement in results between different observers, or occasionally where the party desires to obtain a check on his apparatus and methods. Such tests are in general, however, only made for the several Departments of the Government.

In what follows, I shall attempt to give, as briefly as possible, an idea of the investigations that have been completed, together with the reasons why they were undertaken, and the more important conclusions to which these investigations have led; also a brief statement of some of the more important problems that are now engaging our attention. Those interested will find more detailed information in the original papers to which reference is made in the foot-notes.

*Optical Pyrometry.*<sup>1</sup>—One of the first investigations taken up after the organization of the laboratories was a study of the sources of error of and the order of accuracy attainable with optical and radiation pyrometers, in which the temperature of an incandescent body is estimated from the amount of light or heat emitted by it. The investigation showed that instruments of this type were thoroughly practical and could, under proper conditions, be used to measure the highest attainable temperatures, and the several types of pyrometers examined were found to give results that were still in excellent agreement at the extreme temperature of the electric arc.

While this method of pyrometry is finding a rapidly increasing application in the measurement and control of temperatures with the range of thermoelectric, resistance, and other types of pyrometers, its special field of application is in the measurement of temperatures of inaccessible or moving objects, in the estimation of temperatures beyond the range of any pyrometers requiring contact with the hot body or where such contact would be detrimental to the pyrometer, and in the rapid examination of surfaces for uniformity of heating, a problem of great importance in metallurgical processes. The great advantage of the optical method of temperature measurement lies in the rapid variation in the intensity of the emitted light with variation in temperature. Thus, for example, the intensity of light (red) emitted by a body at  $1500^{\circ}$  C. is over 130 times, and at  $2000^{\circ}$  C. over 2100 times, as great as  $1000^{\circ}$  C. It is this fact alone that makes it possible for the trained eye to estimate, unaided, the approximate temperature in the many industrial processes dependent on temperature control.

It would therefore appear that a system of pyrometry based on the intensity of the light emitted by incandescent bodies would be an ideal one, inasmuch as a comparatively rough measurement of the photometric intensity would fix the tem-

<sup>1</sup> Given in abstract before the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, Detroit Meeting June 28, 1909.

<sup>1</sup> C. W. Waidner and G. K. Burgess, *Bull. Bur. of Stands.*, **1**, 189-254 (1904-5), reprint No. 11.

perature quite accurately. This, however, is only partially true; it is limited somewhat by the fact that different bodies, although at the same temperature, emit vastly different amounts of light. Thus, the intensity of the radiation from incandescent iron or carbon at  $1000^{\circ}\text{C}.$ , for example, is many times greater than that emitted by such substances as magnesia or polished platinum at the same temperature. Consequently if any conclusions were drawn as to the temperatures of these bodies from the light that they emit, it might lead to large errors. Thus, at  $1500^{\circ}\text{C}.$  this difference in the intensity of the light emitted by carbon and by polished platinum would lead to a difference in the estimated temperatures of these bodies of about  $90^{\circ}\text{C}.$ , and less at lower temperatures. The possible erroneous conclusions that might be drawn from such a system of optical pyrometry are still further emphasized in considering the results to which it would lead if applied to the measurement of the temperatures of flames. Here the intensity of the light would vary with the thickness of the flame in the line of sight. If applied to the estimation of the temperature of a colorless Bunsen flame the method would fail entirely.

At first sight the difficulties here enumerated, incident to the different emissivities of bodies being a function not of the temperature alone, but dependent on other properties, such as conditions of surface and materials entering into composition, might seem insurmountable, and sufficient to condemn the use of optical pyrometry. Such, however, is fortunately not the case. It is therefore necessary to consider briefly the principles on which optical pyrometry is based, its limitations, advantages, and the necessary precautions that must be observed in overcoming these difficulties.

There is one type of body, which is generally termed the "black body," whose radiation is entirely independent of the material of which it is made and depends only on its temperature. It should be said that the name "black body" has nothing to do with the color of the body, the body may be at white heat and yet it would be a "black body" in the sense here understood. Inasmuch as a body fulfilling these conditions must absorb all radiation, both visible and invisible, incident on it and must not reflect or transmit any, a condition which is approximately fulfilled by ordinary black surfaces, such a body has received the name of black body, although to avoid the confusion of ideas referred to above, some writers call such a body by other names, such as a "total radiator," a "complete radiator," etc. No body is known whose surface radiation is exactly that of a black body. The radiation from carbon, oxidized iron, black oxides, etc., approximates fairly closely to black body radiation, while the radiation from polished platinum, white oxides, the clean surface of molten copper, iron, etc., is very much less.

Kirchoff first showed that the radiation within an enclosure, the opaque walls of which are at a uniform temperature, is black body radiation. The radiation coming out through a small opening in the walls of such an enclosure is a very close approximation to black body radiation. Up to about  $1600^{\circ}$ , black body radiation may be most conveniently obtained in the laboratory by means of an electric furnace<sup>1</sup> consisting of a porcelain or magnesia tube, suitably protected against excessive heat losses by surrounding tubes and air jackets, which is wound with a platinum ribbon heating coil, and the temperature of which can thus be maintained constant for long intervals by suitable regulation of the electric heating current. The radiation coming out of the end of this tube from an object in contact with a standardized thermocouple at the uniformly heated region near the center of the tube is therefore a very close approximation to black body radiation at a known temperature.

<sup>1</sup> Such complete black bodies, of the form devised by Lummer and Kurlbaum, may be obtained from the Royal Berlin Porcelain Works. Platinum ribbon 2 cm. wide  $\times$  0.01 mm. thick, suitable for the heating coil, may be obtained from any of the platinum refiners.

perature. For temperatures above  $1600^{\circ}$  a carbon tube or other type of electric furnace must be used. All bodies, *e. g.*, carbon and platinum which emit such vastly different amounts of radiation when heated out in the open, when placed within such a nearly closed and uniformly heated region, will emit identically the same radiation. Of all bodies, the black body emits the greatest amount of radiation at a given temperature. It is observed that crevasses in a heated plate appear much hotter than the neighboring surfaces. While this is often in part due to the fact that the interior is at a somewhat higher temperature than the surface, it is to a greater extent due to the fact that the radiation from the small enclosures is approximately black body radiation.

Radiation pyrometers are calibrated in terms of the radiation from a black body, as this radiation alone is a function of the temperature only. They will then give true temperatures only when used on black bodies. When used to measure the temperature of other bodies the radiation pyrometer calibrated in this way will not give the true temperature but the "equivalent black body temperature," *i. e.*, the temperature a black body must have to send out radiation of the same intensity and of the same kind. Two bodies having the same black body temperature may differ very considerably in their true temperatures; thus in the illustration already cited for carbon and platinum at  $1500^{\circ}\text{C}.$ , the difference is of the order of  $90^{\circ}$ . The temperature of a piece of platinum at  $1500^{\circ}\text{C}.$  (as measured by a thermocouple) will, if measured by an optical pyrometer using red light, appear to be about  $1365^{\circ}\text{C}.$ , and if green and blue light are used in the photometry, about  $1405^{\circ}$  and  $1425^{\circ}$ , respectively, showing that platinum approximates more nearly to black body radiation for green and blue than for red light.

The great objection to the use of radiation pyrometers, that their indications are not dependent on the temperature alone but also on the widely varying emissivities of different bodies, may then be answered as follows: these pyrometers can be used to measure the equivalent black body temperatures, and it is then possible to pass over to true temperatures by means of such data as those given below, giving the departure from black body radiation. Further, in many cases arising in industrial operations requiring the use of a pyrometer, the body whose temperature is to be measured is not out in the open but is found enclosed in a furnace whose walls are at a temperature not far different from that of the body, so that the radiation is a fair approximation to black body radiation, and the indications of the radiation pyrometer will not differ much from true temperatures. In many other cases, *e. g.*, when the problem at hand is the measurement of the temperature of an enclosed furnace or of a fused metal bath, the difficulty may be overcome by immersing in the bath or furnace a closed end porcelain or iron tube and observing the radiation coming out of the open end of this tube, in which case the indications of the radiation pyrometer will give true temperatures.

Often a knowledge of the black body temperature fulfils every requirement of the problem at hand, whether it be the control of temperature in an industrial operation or a scientific experiment, and this a radiation pyrometer gives with a very satisfactory precision.

The temperature of any body as measured by a radiation pyrometer will in general (luminescence effects excluded) be lower than its true temperature. There is a source of error, however, that may act in the direction of making the pyrometer read too high, namely, that due to light reflected by the body whose temperature is being measured, coming from surrounding flames and hotter objects. This source of error can often be avoided by screening off such light.

The pyrometers in general use to-day are of two types, one, known as *optical pyrometers*, which are simply photometers, in which the intensity of the emitted light of a single color (*i. e.*

monochromatic light) is compared with the light of the same color from a standard source; the other type, known as *total radiation pyrometers*, in which the total energy radiated, both visible and invisible, is used.

The use of monochromatic light obviates the difficulties incident to the photometry of lights of different color, and further makes it possible to utilize in the calibration of these instruments Wien's equation for the distribution of energy in the spectrum of a black body

$$J = c_1 \lambda^{-5} e^{-c_2/\lambda T}$$

where  $J$  is the intensity of the light of wave-length  $\lambda$ ,  $T$  is the absolute temperature,  $e$  the base of the natural system of logarithms, and  $c_1$  and  $c_2$  constants.

This may be written:

$$\log J = K_1 + K_2 \cdot 1/T$$

where  $K_1 = \log c_1 - 5 \log \lambda$  and  $K_2 = c_2 \log e$ .

If working with visible radiation, it therefore requires only two photometric measurements at two known absolute temperatures to permit of determining the constants,  $K_1$  and  $K_2$ , and so completely standardizing a pyrometer. For infra-red monochromatic radiation a dispersing apparatus (non-absorbing) must be used in connection with a bolometer, thermopile, or other instrument for detecting radiation. For long wave-lengths and high temperatures, Wien's equation ceases to hold, and use must be made of Planck's equation,

$$J = c_1 \lambda^{-5} \left( \frac{c_2}{e^{\lambda T} - 1} \right)^{-1}$$

which the researches of Lummer and Pringsheim, Paschen, and Rubens and Kurlbaum have shown satisfies the experiments for black body radiation throughout the widest range of accurately measurable temperatures ( $-200^\circ\text{C.}$  to  $+1500^\circ\text{C.}$ ) and wave-lengths (to  $\lambda = 51.2 \mu$ ). For the wave-lengths of the visible spectrum, however, Wien's equation represents the results of experiment with every required degree of precision, since for values of  $\lambda T$  not exceeding 3000, Wien's and Planck's equations differ by less than 1 per cent. The former may, therefore, within the visible spectrum, be used for extrapolation to the highest attainable temperatures ( $4000^\circ$  or more).

The Stefan-Boltzmann equation for the energy of total radiation is

$$E = K(T^4 - T_0^4)$$

where  $E$  is the energy of total radiation, visible and invisible,  $T$  the absolute temperature of the radiating black body source,  $T_0$  that of the receiving instrument, and  $K$  a constant. This method can be used to measure temperatures of bodies even long before they become incandescent.

For this purpose such instruments as the bolometer of Langley, Crookes' radiometer as modified by Nichols, the actinometers of Pouillet and Violle, the radiomicrometer of Boys, and the thermopile may be used.

Féry and Thwing have recently brought out practical instruments based on the energy of total radiation, which is measured by the rise in temperature produced at one junction of a very sensitive thermocouple joined to a direct reading pyrometer galvanometer.

The Stefan-Boltzmann equation has a very strong theoretical as well as experimental basis. The Planck equation has also been deduced theoretically from the electromagnetic theory of radiation, but the theoretical deduction involves certain assumptions which are not the only possible ones, so that it cannot be said to rest on as solid a theoretical basis as the former equation, although thus far, it has satisfied very well every experimental test to which it has been subjected.

The types of pyrometers that have been carefully investigated, examples of which are being regularly standardized in our laboratories, are the Le Chatelier, the Féry, the Wanner, the Morse, and the modified form of the latter originally put out

under the name of the Holborn-Kurlbaum, optical pyrometers and the Féry thermoelectric telescope, the Féry concave mirror and the Thwing total radiation pyrometers.

In the Le Chatelier optical pyrometer the light from a small area of a gasoline flame, burned at standard height, illuminates one-half of the photometric field and light from the incandescent body under observation, the other half of the field. Approximately monochromatic light is obtained by means of a red glass before the eye-piece. The two contiguous halves of the photometric field are brought to equal brightness by a variable cat's eye diaphragm, provided with a graduated scale, and placed before the objective lens of the telescope in the path of the light from the incandescent body. To avoid working with too small openings of the diaphragm at high temperatures, glasses of known absorbing power are placed in front of the diaphragm, and for the lower range of the instrument similar glasses are interposed in the path of the light from the standard lamp. The effects of time of burning of the standard lamp, of variations in the height of flame, of using different gasolines, of errors in focusing on the incandescent body, of observations by different observers, etc., were carefully investigated. The errors from all these causes are such that an accuracy of 1% in temperature measurements is readily possible, and a somewhat higher accuracy with sufficient care. The chief advantages of the Le Chatelier pyrometer are that it is self-contained and it is much cheaper than some of the other optical pyrometers. For use in schools, where first cost is often of prime consideration, it will serve very well to illustrate the fundamental principles of optical pyrometers and their calibration by use of the Wien equation. While the accuracy attainable is about as good as with the more recent forms of optical pyrometers, it has some disadvantages for shop use, in that it can only be sighted in a horizontal direction, and when used where there are air draughts the constant movement of the flame of the standard lamp, causing its portion of the photometric field to be alternately light and dark, is very annoying.

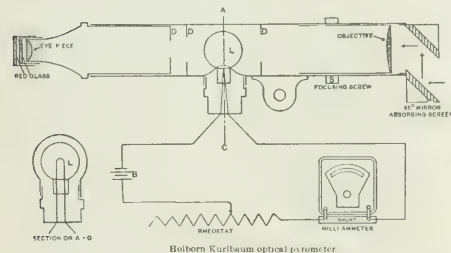
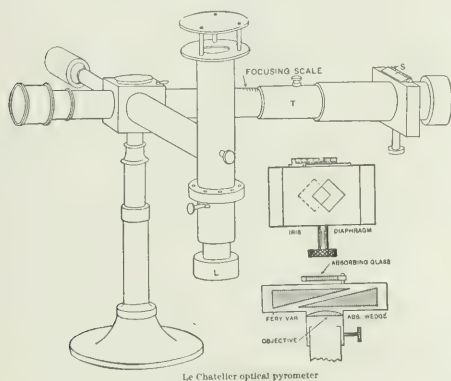
Féry, in his absorption pyrometer, which is very similar to the Le Chatelier, has incorporated some practical improvements. The standard gasoline lamp is retained. Light from this lamp illuminates the central strip of the photometric field and light from the incandescent body the two strips on either side. The cat's eye diaphragm of the Le Chatelier pyrometer is replaced by two wedges of absorbing glass, the thickness, and therefore the absorbing power, of which can be varied by sliding one wedge over the other. The pyrometer can be turned around on both horizontal and vertical axes. The sources of error and the accuracy attainable are about the same as for the Le Chatelier pyrometer. The standard lamp is provided with a glass chimney and is somewhat less affected by air draughts than in the latter instrument. To avoid the inconveniences incident to the use of the lamp, we have tried, with satisfactory results, replacing the gasoline lamp with an incandescent lamp, which was used to illuminate a matt surface placed in fixed relation to the lamp, which surface then becomes the standard source of light. In this case, however, it is necessary to set the incandescent lamp to standard brightness as is done with the Wanner pyrometer.

The Wanner pyrometer is also simply a photometer, though differing greatly in mechanical details of construction from the two former types of pyrometers. A small 6-volt incandescent lamp serves as the standard light which illuminates one-half of the photometric field, the light from the incandescent body illuminating the contiguous half of the field. In this pyrometer red glasses are dispensed with and light which is more nearly monochromatic is obtained by spreading the light out into a spectrum and cutting out a narrow band in the red by a suitable slit diaphragm. To enable the two photometric fields to be brought to the same brightness, the two beams of light, from the standard incandescent lamp and the hot body respec-

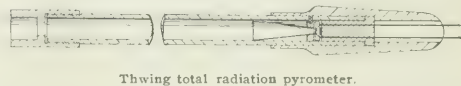
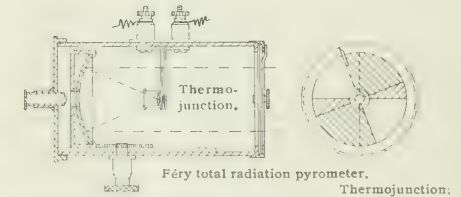
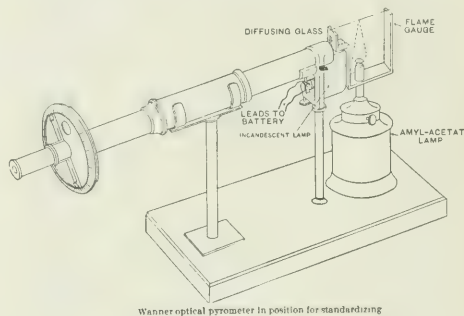


tively, are first polarized in planes at right angles by means of a Rochon prism, and are then passed through a Nichol prism before the eye-piece. By turning the Nichol, one or the other beam of light may be increased or diminished until a photometric match is obtained. The position of the Nichol is read off on a circular graduated scale which is calibrated in terms of black body temperatures. The small incandescent lamp which serves as the working standard of light in this pyrometer is run from a small three-cell storage battery, the e. m. f. of which will, of course, vary with its state of charge, which, if uncontrolled, would cause large variations in the light standard. To avoid this source of error, the electric lamp is set to standard brightness each morning, before beginning work with the pyrometer, by mounting the pyrometer in its holder before a small lamp burning pure amyl acetate, the flame being set to standard height by the flame gauge, and the pyrometer being sighted on a definite portion of the flame, and with the index of the Nichol set at a definite reading called the standard reading

a millimeter in circuit with the lamp. This method has since been adopted by the makers of this pyrometer. When this precaution is taken the accuracy attainable with the Wanner pyrometer is entirely satisfactory, being about the same as with the instruments previously described, *viz.*, 1% in temperature. When used in this way, in connection with a millimeter, the comparison with the amyl acetate lamp need only be made once or twice a week as the deterioration of the incandescent lamp, at the temperature at which it is burned, is very slow. For the measurement of very high temperatures an absorbing glass is used, as in the case of the pyrometers already described. On account of the great loss of light in the optical parts, the original Wanner instrument could not be used below about 900° C. The makers have recently brought out a modified form which is adapted to the measurement of temperatures as low as about 675° C. What is sometimes a disadvantage in this pyrometer is the fact that it is not a telescope, like the other pyrometers, and it is thus difficult to be



(Normalzahl). The current through the electric lamp is then varied by a simple rheostat until the photometric field illuminated by the electric lamp is exactly equal in brightness to the adjacent photometric field illuminated by the standard amyl acetate flame. If then the battery is in good condition the pyrometer may be used throughout the day. If, however, the battery is not in good condition, or there are bad electrical contacts in the circuit, the current through the lamp may change in the course of a day's work and cause very considerable errors. A very small change in current through an incandescent lamp causes a very marked change in brightness, a change of 1% in current corresponding to about 6% in brightness or nearly 1/2% in temperature. Hence, as the normal working current through the lamp is about 0.6 ampere, in order to obtain a precision of 1/2% at 1000° C. (*i. e.*, 5°), the current must remain constant to within 0.006 ampere. To assure his constancy of current, we have used in our experiments



sure of the exact spot that is under observation on the incandescent body. It also requires a considerable area on which to sight so that it is not possible to measure the temperature of so small an object as with the Féry absorption pyrometer, for example. Its advantages are that the pyrometer itself is quite light and portable; although the batteries and milliammeter must also be carried around with the pyrometer, it can be readily sighted at any angle, is undisturbed by air currents, and is well adapted for the rapid examination of a large surface for uniformity of heating.

Morse has introduced a new and ingenious method in his pyrometer which he calls the Thermo Gage. An incandescent lamp, mounted in a darkened tube open at the ends, is interposed between the eye and the incandescent body under observation. The current through the lamp is then varied by a suitable rheostat until a selected part of the filament is of the same brightness as the incandescent background, when it completely merges.



with the latter and fades from view. The current through the filament, under these conditions, is read on a milliammeter and serves as a measure of the temperature of the incandescent body, after the lamp has been once calibrated by observations on a black body. Even in this simple form, this pyrometer is capable of giving results of great precision. In the type of instrument formerly known as the Holborn-Kurlbaum, which uses Morse's disappearing filament principle, a small 4-volt incandescent lamp is used, and an objective lens is placed in front of the lamp so that an image of the incandescent body whose temperature is to be measured is formed in the plane of the lamp filament, which is then viewed with a simple magnifying eye-piece. For measurements above about  $1600^{\circ}\text{C}$ ., to avoid burning the lamps at high temperatures, absorbing glasses are used between the lamp and the hot body. After carefully selected lamps, having quite uniform brightness over a considerable length of the filament, are aged by burning for about 20 hours at  $1800^{\circ}\text{C}$ ., their subsequent changes during many hundreds of hours are quite small, since, by use of suitable absorbing glasses, it is never necessary to burn them at temperatures above  $1500^{\circ}\text{C}$ . or thereabouts. The constancy of these lamps, for the purposes of temperature measurement, will be readily understood when we remember that an ordinary incandescent lamp will burn some 600 or 800 hours at 3.5 watts per candle, corresponding to about  $1850^{\circ}\text{C}$ ., before its candle-power drops to 80% of its initial value. If burned at only  $1500^{\circ}\text{C}$ ., it would take some thousands of hours before the candle-power decreased by 20%, which corresponds to a temperature change not exceeding  $1-1\frac{1}{2}\%$  (*i. e.*,  $15^{\circ}$  at  $1000^{\circ}$ ). The small lamps would probably have a somewhat shorter life, however, than the average 110 volt lamp. A somewhat higher accuracy can be obtained with this pyrometer than with any of the others, about  $\frac{1}{2}\%$  in temperature. It is very convenient to use, and if a small lamp is used, so that three storage cells will suffice, it is about as portable as the Wanner pyrometer. It can be used for the measurement of the temperature of very small objects.

In the Féry thermoelectric telescope the radiation, both visible and invisible, is focused on a minute thermojunction made of iron (or copper) and constantan wires about 0.001 inch in diameter, and the thermoelectric current thus produced is observed with a suitable galvanometer. Fluorite was chosen for the lens because it transmits the longer heat waves with very small absorption, so that the deflections of the galvanometer, which are very approximately proportional to the energy received by the thermopile, will thus be proportional to the 4th power of the absolute temperature according to the Stefan-Boltzmann law, if the radiating source is a black body. As only small lenses of fluorite can be obtained at any cost, the amount of energy concentrated on the thermojunction is very small and requires a rather more sensitive galvanometer than can be conveniently adapted to shop use. To overcome this objection Féry has replaced this lens by a much larger concave mirror (about 7.5 cm. diameter), with a gold-plated reflecting surface, so that a much larger amount of radiant energy is concentrated on the thermocouple, thus making it possible to use a more robust and portable galvanometer. This pyrometer, which is known as the Féry radiation pyrometer, has found considerable application in the industries. An arrangement is provided by means of which an image of the hot body is focused on the small blackened silver disk, in the axis of the mirror, to which the thermocouple wires are soldered. The image must completely cover the disk. To do this requires, with the usual form of instrument furnished, an area of the hot body having a diameter of 2 to 3 cm. for each meter that the pyrometer is distant from the hot body. If then, for example, in the use of the pyrometer, black body conditions are realized by means of a closed end tube extending into the fur-

nace and the pyrometer is focused on the bottom of this tube, care must be taken that the cone of rays from the surface whose temperature is sought to the concave mirror is nowhere intercepted by the walls of the tube. The galvanometer furnished with this pyrometer is generally provided with two scales, one extending from about  $400^{\circ}$  or  $500^{\circ}$  to  $1100^{\circ}\text{C}$ . or thereabouts, and the other from about  $1100^{\circ}$  to  $1800^{\circ}\text{C}$ . For the higher range a sector disk is mounted in front of the pyrometer, which thus reduces the effective area of the concave mirror by a known amount. By suitably choosing the area of opening in the disk, the scale of the instrument can be extended to any temperature, however high. By the use of a suitable recorder this pyrometer can be used to give a continuous record of the temperatures. This pyrometer has a large field of usefulness in many industrial operations. Its application, however, has frequently been attempted where the conditions were unfavorable to its use and where other pyrometers are more suitable.

Thwing has also recently brought out a pyrometer based on the measurement of the energy of total radiation. In a steel tube, with blackened interior, about 90 cm. long and 2.5 cm. diameter, a minute iron-constantan thermojunction is mounted, about 70 cm. from the open end, at the apex of a metal cone which serves to concentrate the energy of radiation upon the junction, after a series of multiple reflections. The front end of the tube has a circular diaphragm which, with the aperture of the cone, serves to define a beam of radiation of constant angular aperture, so that the pyrometer will be in focus at all distances if the area of the hot surface under observation is sufficiently large to completely fill this angle. The thermocouple is connected to a suitable pivot galvanometer, of quite robust construction, which serves to measure the rise in temperature of the hot junction of the couple, and thus the energy of radiation from the hot body.

The presence of water vapor, carbon monoxide, and carbon dioxide gases, which are always present in furnaces, causes the total radiation pyrometers to read low on account of the strong absorption of these gases for certain of the longer waves of the spectrum. Dense fumes may, of course, cause them to read far too low. Like all optical pyrometers they will give the "equivalent black body temperature" of the body under observation. By the "equivalent black body temperature" here is meant the temperature at which a black body would send out total radiation (visible and invisible) of the same intensity as is actually sent out by the body under observation; just as before, when using optical pyrometers and red light, the equivalent black body temperature was the temperature at which a black body would send out red light of the same intensity as the body in question. These two black body temperatures are not equal. The black body temperature measured from the total radiation is in general lower than that measured by the emitted light. When these pyrometers are applied in foundry work to the measurement of temperatures of molten metals, they may give readings many hundred degrees too low. This point will be referred to again in connection with the estimation of the temperature of copper by means of optical pyrometers.

The optical pyrometers were applied to a study of the radiation from a number of substances, including platinum, iron oxide, copper oxide, fire clay and unglazed porcelain. For platinum, at  $700^{\circ}$ ,  $1000^{\circ}$ ,  $1300^{\circ}$  and  $1600^{\circ}\text{C}$ ., the equivalent black body temperatures, for red light, were  $662^{\circ}$ ,  $921^{\circ}$ ,  $1191^{\circ}$  and  $1464^{\circ}$  respectively. At  $1000^{\circ}$ ,  $1300^{\circ}$ , and  $1600^{\circ}\text{C}$ ., the equivalent black body temperatures, for green light were  $929^{\circ}$ ,  $1213^{\circ}$  and  $1497^{\circ}\text{C}$ . respectively. At  $1300^{\circ}$  and  $1600^{\circ}\text{C}$ ., the equivalent black body temperatures for blue light, were  $1237^{\circ}$  and  $1525^{\circ}\text{C}$ . respectively. This shows that platinum is a very selective radiator, approaching much more nearly to

black body radiation for blue and green than for red radiation. This question of selective radiation, as will be seen later, is of great importance in the question of the efficiency of artificial illumination. The black body temperatures of platinum at the instant of melting, measured with red, green and blue light, was found to be  $1541^{\circ}$ ,  $1577^{\circ}$  and  $1612^{\circ}$  C. respectively. The true temperature of the melting point of platinum, as will be seen later, is over  $1750^{\circ}$  C. Certain substances like platinum, silver, gold, clean surface of molten metal, etc., emit light which is partially polarized, the amount of polarization being nil in a direction perpendicular to the radiating surface and increasing with the angle at which the surface is viewed. Readily oxidizable substances, and substances like porcelain, carbon, glass, etc., emit only small percentages of polarized light. In pyrometers which use polarized light, like the Wanner, very appreciable errors are possibly due to the above facts. Thus in some temperature measurements on a platinum strip, at  $1450^{\circ}$  C., made with a Wanner pyrometer, and viewed at angles of 30, 50 and 70 degrees, the extreme differences in the pyrometer readings for positions of the pyrometer at right angles were  $34^{\circ}$ ,  $80^{\circ}$  and  $90^{\circ}$  C. respectively. The possible errors due to the emitted light being polarized are therefore one-half of these observed differences. This source of error can always be avoided by viewing the surface normally or by taking the mean of four readings of the pyrometer in positions at right angles to one another. The effective absorption of the absorbing glasses used with optical pyrometers will also be different for different positions of the surfaces of these glasses with respect to the radiating surface, if the emitted light is polarized.

*Radiation from Platinum at High Temperatures.*<sup>1</sup>—This paper contains a theoretical discussion and deduction of certain corollaries to Wien's equation for monochromatic radiation and their application to the data found in the preceding investigation on the monochromatic radiation from platinum.

*On the Temperature of the Arc.*<sup>2</sup>—After calibration by observation on a black body at temperatures up to  $1500^{\circ}$  C., and the determination of the coefficients of absorption of a number of absorbing glasses, the Le Chatelier, the Wanner and the Holborn-Kurlbaum optical pyrometers were applied to a determination of the temperature of the hottest portion of the positive crater of the electric arc, with a view, primarily, to determining the consistency with which such extreme temperatures could be measured with the different pyrometers, and also to see how measurements of temperature based on the Wien-Planck equation for monochromatic radiation would agree with measurements based on the Stefan-Boltzmann law for total radiation. The determinations which were made using both red and green light, gave  $3700^{\circ}$  absolute<sup>3</sup> "black body temperature," with a maximum variation of only about  $20^{\circ}$  from the mean for the several pyrometers. This result based on the Wien-Planck equation is in fairly satisfactory agreement with a determination by Féry ( $3760^{\circ}$ ) based on the Stefan-Boltzmann law, thus indicating that the radiation laws are still in quite satisfactory agreement at this extremely high temperature.

When the current through the carbon (13 mm. diameter) was increased from 15 to 22 amperes there was an increase of  $44^{\circ}$  in the temperature of the positive crater, and on increasing the current to 30 amperes a further rise in temperature of  $34^{\circ}$ . In these experiments the current was varied without the knowledge of the observer taking the temperature measurements and the effect was always found in the many hundreds of measurements made by different observers and with different types of pyrometers. These results are in contradiction to the experiments of Violle and others, who found no varia-

tion in temperature with variation in current. Violle remarks "the brightness of the positive carbon is rigorously independent of the electric power expended to produce the arc, changing from within the limits of 10 amperes at 500 watts to 400 amperes at 34000 watts." As this experimenter used larger carbons for the larger arcs, the effect might have been masked due to this cause. In view of the fact that the Holborn-Kurlbaum pyrometer is so peculiarly well adapted to rapid observations on the small area of the crater, permitting the wandering of the hottest spot to be followed with great certainty, and from the fact that almost identical results were found with the Le Chatelier pyrometer under conditions of use where the eye received light only through a 1 mm.<sup>2</sup> opening of the cat's eye diaphragm of the pyrometer, so that greater brightness of the surrounding field due to increase in crater area with current could not influence the eye, we felt reasonably certain that an increase in current is accompanied by a rise in the temperature of the crater.

Electrodes of pure Acheson graphite gave a temperature about  $40^{\circ}$  higher than the carbon electrodes. There is a very marked change in temperature with change in the kind of carbon used. Wanner states that cored carbon electrodes give a temperature about  $170^{\circ}$  lower than solid retort carbon. For these reasons the attempts to use a small screened area of the positive crater of the arc as a primary standard of light have not been successful. Blondell has found for four different qualities of homogeneous carbons an average value of 158 candles per mm.<sup>2</sup> for the brightness of the hottest part of the positive crater, the values ranging from 150 to 163. With cored carbons he obtained values lower than 130.

*The Radiation from and the Melting Points of Palladium and Platinum.*<sup>1</sup>—In this investigation the melting points of platinum and palladium were determined by several different methods. In one method, called the black body method, a wire of the purest palladium or platinum was placed at the center of an electric furnace, the heating tube of which was of pure iridium. The temperature of the furnace was very slowly raised, as the melting point of the metal was approached, by suitable regulation of the electric heating current, and observations of the radiating disk at the center of the furnace and in contact with the wire were taken with a Holborn-Kurlbaum optical pyrometer, accompanied by simultaneous time readings. The instant of melting of the platinum wire was detected by the interruption of an electric circuit, and from the temperature-time plot the temperature corresponding to the instant of melting was obtained. A large number of determinations of the melting point were thus made, with different absorbing glasses or rotating sector disks before the pyrometer, with a number of different pyrometer lamps which had been carefully standardized against a specially constructed black body having a very uniform temperature throughout a large region, and with red, green and blue light. From the Wien equation we have

$$\log K = c_2 \log c \left( \frac{1}{T_1} - \frac{1}{T_2} \right),$$

where  $K$  is the coefficient of absorption of the absorbing glasses or the rotating sector disk,  $c_2$  the constant of the Wien equation,  $e$  the base of the Napierian logarithms,  $\lambda$  the wave length of the light used,  $T_1$  the apparent absolute temperature of the black body furnace as given by the optical pyrometer when the absorbing glass or sector disk is interposed, and  $T_2$  the absolute temperature of the black body furnace.  $T_2$  being the only unknown quantity in this equation, is thus determined. The value taken for  $c_2$  was 14,500. The object of using absorbing glasses and rotating sector disks is to reduce the observed readings of the optical pyrometer below  $1200^{\circ}$  or thereabouts,

<sup>1</sup> G. K. Burgess, *Bull. Bur. Stand.*, **1**, 443-447 (1904-5), reprint No. 24.

<sup>2</sup> C. W. Waidner and G. K. Burgess, *Bull. Bur. Stand.*, **1**, 109-124 (1904-5), reprint No. 8.

<sup>3</sup> i. e.,  $^{\circ}$ C. +  $273^{\circ}$ .

<sup>1</sup> Waidner and Burgess, *Bull. Bur. Stand.*, **3**, 163-208 (1907), reprint No. 55.

inasmuch as the standard scale of temperature, as determined with the gas thermometer, has not, up to the present time, been extended above this temperature with any certain accuracy. In this connection it should be remarked that some determinations of the melting point of palladium made without any absorbing glasses, and assuming that the lamp calibration equation of the optical pyrometer, based on observations in the interval of accurately known temperatures from 650° to 1200° C., still continued to hold at the melting point of palladium, some 350° higher, and gave results differing by only a few degrees from those obtained by the above method.

The surface radiation from palladium and platinum, which is practically identical for both metals, was studied by three different methods, for temperatures from 650° to 1400° C. and for red and green light. The methods used and the results obtained will be found in the published paper referred to. Observations with the optical pyrometer on ribbons of platinum at the instant of melting, which was accomplished by slowly increasing the electric current through the ribbon, gave for the black body temperature of platinum at the melting point 1539° C. for red light and 1585° C. for green light. From the experiments, referred to above, on the radiation from platinum in the interval 650°-1400° C., the necessary data were at hand to pass from the observed black body temperatures to the true temperature of melting, assuming that the platinum surface conserves its properties at higher temperatures up to its melting point. While this method of determining the melting point is entitled to far less weight than the black body method, it is interesting to note that the determinations using red light gave 1748° and those with green light 1757° C., the mean of which is identical with the results obtained by the black body method and the use of the Wien equation.

The final results of this investigation are:

Melting point of palladium = 1546° C.

Melting point of platinum = 1753° C.

Nernst and Wartenberg, using the black body method and a Wanner optical pyrometer adjusted for yellow light, found for palladium 1541° and for platinum 1745°, when the constant of the Wien equation was taken as  $c_2 = 14,600$ . Holborn and Valentiner, in an elaborate intercomparison of the optical temperature scale with the scale of their iridium bulb gas thermometer, found for the constant of the Wien equation,  $c_2 = 14,200$ , and for the resulting melting points of palladium and platinum, 1582° and 1789° C., respectively.

The large discrepancies in the values of these melting points, as found by the different observers, are to a great extent only apparent rather than real, being due to the different values assigned to the constant  $c_2$ . For example, if the above determinations of the platinum melting point are all reduced to the same value of  $c_2 = 14,500$ , they become: Nernst and Wartenberg 1751°; Holborn and Valentiner 1770°; Waidner and Burgess 1753°. On account of the uncertainty in the value of  $c_2$ , further work must be done on the determination of this constant.

Determinations of the melting points of palladium and platinum were also made by the thermoelectric method, using ten couples of the following percentage composition: Pt, 90 Pt-10 Rh; Pt, 90 Pt-10 Rh, 80 Pt-20 Rh; Ir, 90 Ir-10 Ru. In the experiments on palladium the e. m. f. of the couple was noted at the instant of melting of a short piece (3 to 6 mm.) of Pd wire which was fused between the junctions of the thermocouple. In the experiments on platinum a similar procedure was followed with the 90 Pt-10 Rh, 80 Pt-20 Rh couples. With those couples in which one wire was itself of pure platinum, the e. m. f. at the instant of melting of this wire at or very near the junction was observed. The wires were melted in an iridium furnace, the temperature of which was slowly raised until the wire melted. The couples were calibrated in the usual way by observations at the freezing points of zinc (419°), antimony

(630.5°), and copper (1084°), from which the constants of the equation

$$e = a + bt + ct^2$$

were computed,  $e$  being the e. m. f. of the couple when the hot junction is at a temperature  $t$ , and the cold junction is at 0° C., and  $a, b, c$  being constants. Assuming then that the equation continues to hold up to the melting point of platinum, this method gave with the platinum alloy couples 1530° and 1706° C. as the melting points of Pd and Pt, respectively, values which are in very good agreement with the determinations, by the same method, of Holborn and Henning, *viz.*, 1530° and 1710°, and by Harker, *viz.*, 1710°. It will be observed that this method gives a much lower value for the melting point of platinum than the radiation method (1753°). In this connection we would remark that the thermoelectric method can hardly be considered at all as a method of determining the melting point of platinum for we have no reason to expect that the above purely empirical calibration equation of the couple, found to hold between 419° and 1084°, will continue to hold when extrapolated over 600°. The fact that different couples of iridium and rhodium alloys with platinum agree remarkably well when thus extrapolated, is not proof that this equation continues to hold good, for when other couples were used, *e. g.*, the iridium, iridium-ruthenium couple, different results were found. Furthermore, when, for the platinum couples, another calibration equation was used, *e. g.*, the Holman equation  $e = mt^n$ , different results were obtained. Thus, using this equation, which holds within the calibration interval 419°-1084° almost as well as the other formula, and determining the constants  $m$  and  $n$  by observations at the freezing points of zinc and copper, the values 1544° and 1732° were found for Pd and Pt, respectively. When the constants were determined by observations at the freezing points of antimony and copper, the values 1542° and 1730° were found.

The temperature scale quite generally used to-day, up to 1600° or 1700° C., is that defined by platinum thermocouples, calibrated at the freezing points of zinc, antimony, and copper, and an extrapolation of the equation  $e = a + bt + ct^2$ . At high temperatures this scale undoubtedly gives too low values for the temperature. The corrections that must be applied to this thermoelectric scale to obtain temperatures on the optical scale resulting from the investigation above described, on which scale the m. p. of Pd = 1546° and the m. p. of Pt = 1753°, are given in the following table:

Temp. on thermoelectric scale . . .	1200°	1 00°	1400°	1500°	1600°	1700°
Optical scale — Thermoelectric scale . . . . .	0°	2°	6°	14°	25°	43°

*Melting Points of the Iron Group Elements by a New Radiation Method.*<sup>1</sup>—In this method a minute specimen of the substance, whose melting point was to be determined, was placed on a platinum ribbon whose temperature was slowly raised by means of an electric current until the specimen, viewed through a microscope, was observed to melt, at which instant the equivalent black body temperature of the platinum ribbon was measured with an optical pyrometer, and the true temperature deduced by means of the data found previously by the experiments on the radiation from platinum. This method is particularly applicable to the determination of the melting points of the rarer refractory elements, and where the pure material can only conveniently be obtained in small quantities, about 0.001 milligram being sufficient for a single determination. The platinum strip was mounted within an enclosure filled with hydrogen to prevent oxidation of the small specimen of metal under observation. Under these conditions a compound of the metal, which could be reduced to the metal by hydrogen, would also serve for determining the melting point of the metal. This method was applied to the metals of the iron group more

<sup>1</sup> G. K. Burgess, *Bull. Bur. of Stand.*, **3**, 345-355 (1907), reprint No. 62



with a view to trying it out than as an accurate determination of the melting points with the highest accuracy. The following results were obtained:

APPROXIMATE MELTING POINTS OF THE IRON GROUP.

Metal.	Melting point.	% Purity.
Iron .....	1505° C.	99.95
Chromium.....	1489	98.99
Cobalt.....	1464	99.95
Nickel.....	1435	99.95
Manganese .....	1207	98.99

These results are expressed on the optical temperature scale as previously discussed, on which scale the melting point of platinum is 1753°. The above values are in excellent agreement with some of the latest determinations by the thermoelectric method, notably Harker's determination of the nickel point, and the determination of Tammann and his associates for iron, nickel, cobalt, and manganese, when their thermoelectric data are corrected and account is taken of the difference between the thermoelectric and optical scales.

*The Estimation of the Temperature of Copper by Means of Optical Pyrometers.*<sup>1</sup>—It has frequently been observed that the temperature indications of optical and radiation pyrometers sighted on the clean, unoxidized surface of molten iron or copper in the ladle are much lower than when sighted on the same metal after it has solidified. This is due to the fact that the emissivity of the clean liquid surface is much less than that of the solid oxidized surface (or of the slag). In order, therefore, to obtain an idea of the true temperatures of molten iron, steel, copper, etc., from the observed indications of optical and radiation pyrometers sighted on the free surface (*i. e.*, not in the furnace, where approximately black body conditions prevail) of these metals, under which condition the pyrometers may in some cases give readings several hundred degrees low, it is as necessary to investigate the emissivities of these substances.

Measurements made with optical pyrometers sighted on clean molten copper surfaces, using red and green light, gave the following results:

Red Light ( $\lambda = 0.65\mu$ )  $t = 1.515r - 359$

Green Light ( $\lambda = 0.55\mu$ )  $t = 1.515g - 477$

where  $t$  is the true temperature Centigrade of the molten copper and  $r$  and  $g$  are the apparent temperatures (*i. e.*, equivalent black body temperatures) given by the optical pyrometer using red and green light respectively. These measurements were made at temperatures ranging from the melting point of copper up to 1200°C. It will be seen from the above equations that at the melting point of copper the pyrometer using red light reads 130°C. too low, and the apparent temperatures with green light are higher than those with red light by a constant amount, *viz.*, 78°C. When the copper freezes or when an oxide coating forms on the liquid, the readings of the optical pyrometer are higher than when the surface is clean. For a thin coating of oxide floating on the liquid the optical pyrometer reads about 100° higher when red light is used and about 35° higher when green light is used, indicating also the relatively greater intensity of the green in the light emitted by liquid copper. The following table gives approximately the true

TEMPERATURES WITH OPTICAL PYROMETERS.

(Red light,  $\lambda = 0.65\mu$ .)

Liquid copper.		Cuprous oxide.	
Pyrometer reading	True temperature Centigrade	Pyrometer reading	True temperature Centigrade
950°	1082°	950°	958°
975	1118	1000	1020
1000	1156	1050	1087
1025	1193	1100	1159
1050	1231	1150	1233

temperatures in terms of the indicated readings of optical pyrometers, using red light, and sighted upon either the clean molten copper or the oxide surface.

With the Fery total radiation pyrometer the difference in readings, when sighted, first on the clear solid copper and then on the oxide, was from 275° to 300°C., and the apparent temperature of freezing when sighted on the clean liquid was slightly less than 600°C. instead of 1080°C. as given by the thermocouple. According to the condition of the copper surface, the corrections to the readings of this instrument lie between about 480° and 175°C. at the copper melting point. The relation between the true temperature and the apparent temperature as obtained with a Fery total radiation pyrometer sighted on a clean copper surface and on an oxide surface is given by the following equations:

Clean liquid copper  $t = 3.55F - 1018$

Cuprous oxide  $t = 1.41F - 169$

where  $t$  is the true temperature Centigrade and  $F$  is the reading of the Fery pyrometer.

The emissivities found for the clean liquid surface of copper and for the cuprous oxide surface, in terms of the emissivity of a black body, are given in the following table, where, under  $\epsilon_x$  is given the emissivity for red ( $\lambda = 0.65\mu$ ) and for green ( $\lambda = 0.55\mu$ ) light and under  $E_x$  the emissivity for total radiation:

EMISSIVITY OF LIQUID COPPER AND OF CUPROUS OXIDE.

Liquid copper.				Cuprous oxide.			
Temp. °C.	$\epsilon_x$			Temp. °C.	$\epsilon_x$		
	red.	green.	$E_x$		red.	green.	$E_x$
1075°	0.17	0.47	0.16	800°	....	....	0.66
1125	0.15	0.38	0.15	900	....	....	0.60
1175	0.14	0.32	0.15	1000	0.80	....	0.56
1225	0.13	0.28	0.14	1100	0.60	0.68	0.54
1275	....	....	0.13	1200	0.49	0.49	....

Thwing has also found 0.14 for  $E_x$  with his total radiation pyrometer sighted on a stream of molten copper. For the clean surfaces of molten cast iron and steel he finds for  $E_x$ , 0.28 and 0.29 respectively.

It is planned to carry out further experiments along these lines, on iron, steel, bronzes, glass, etc.

*Preliminary Measurements on Temperature and Selective Radiation of Incandescent Lamps.*<sup>1</sup>—This investigation was undertaken to determine the reason for the great gain in the efficiency of the new metal filament incandescent lamps (tantalum, osmium, tungsten), just then being developed, over the carbon filament lamp. As is well known, the energy radiated by an incandescent body consists of both the shorter waves of the visible spectrum, which are detected by the eye, and the longer waves of the infra-red portion of the spectrum. The higher the temperature of the radiating body the greater is the proportion of energy associated with the shorter waves of the visible spectrum, but even at the highest attainable temperatures only a few per cent. of the total energy of radiation exists in the form of visible waves, a fact which explains the very low efficiency (1-3%) of all artificial illuminants dependent on purely thermal radiation. One obvious way, therefore, to increase the efficiency of such illuminants is to increase the temperature. Thus if the normal working temperature of the carbon filament is increased by only 150°C., the energy consumed is only increased about one-third while the candle power is doubled; if the temperature is raised to 2700° or 2800°C., at which temperature the filament breaks down in a few minutes, the efficiency is raised to a point where only a fraction of a watt is required per candle power. At a given temperature, the black body radiates more energy per unit area than any other body, yet, while it emits more light also, it is the least efficient of all known sources of illumination because it also emits so

<sup>1</sup> G. K. Burgess, *Bull. Bur. of Stand.*, **6** (1909), reprint No. 121.

<sup>1</sup> C. W. Wainder and G. K. Burgess, *Bull. Bur. of Standards*, **2**, 319-329 (1906), reprint No. 40.



much more of the infra-red radiation. From this standpoint, carbon is not an advantageous substance to use for filaments because its radiation, of all substances found in nature, approaches about as nearly as any to black body radiation. Another method, therefore, of increasing the efficiency of illuminants is to use selective radiators that emit a relatively larger proportion of their radiation in the form of short waves. An ideal substance would be one that could be used at very high temperatures and which would emit only the short waves of the visible spectrum (0.4 $\mu$  to 0.7 $\mu$ ). No purely thermal radiator has this latter property. The nearest approach to this among artificial illuminants is in the electrical excitation of gases, where only certain waves, characteristic of the gas, are emitted. The laws of thermal radiation do not apply to radiation of this kind, which is called luminescent radiation. We have previously seen, from the experiments on platinum, that the radiation of this metal approaches more nearly to black body radiation for the shorter than for the longer waves of the visible spectrum. If, therefore, it continues to depart still more from black body radiation for the longer waves of the infra-red portion of the spectrum, as has since been shown by Coblentz to be the case for platinum, osmium, etc., it is evident that a platinum filament at a given temperature, would be a more efficient illuminant than a carbon filament. This advantage, however, is more than overbalanced by the fact that platinum cannot be used at so high a temperature as the carbon filament. The metals used in the newer metal filament lamps enjoy both of these advantages, *viz.*, that of selective radiation and a high working temperature, and one of the objects of this investigation was to determine whether their much greater working efficiency (than the carbon filament lamp) was due to a higher working temperature or whether it was to a great extent due to selective radiation.

The filaments are so fine that their temperature cannot be readily measured by means of any of the optical pyrometers. The following method was accordingly devised: a carbon ribbon filament, about 4 mm. wide and 4 cm. long, was mounted in an evacuated glass bulb. This filament could be heated electrically to any desired temperature up to 1900° C. The filament of the incandescent lamp, the temperature of which was to be measured, was heated up until it was of the same brightness as the carbon ribbon when viewed against the incandescent ribbon as a background, and the black body temperature of the carbon ribbon was then measured with a Holborn-Kurlbaum optical pyrometer. Measurements were made with red, green and blue glass inserted between the eye and the lamps. From a series of observations at different temperatures an equation was computed of the form  $I = a + bt + ct^2$ , giving the relation between the current,  $I$ , through the filament and its corresponding black body temperature,  $t$ . These measurements gave the following results:

NORMAL BURNING TEMPERATURES

Type of lamp.	Watts per candle.	Observed black body temperature (red).	Approximate true temperature.
Carbon.....	4.0	50	1710° C.
Carbon.....	3.5	118	1760°
Carbon.....	3.1	118	1860°
Tantalum.....	2.0	110	1865°
Tungsten.....	1.0	100	2135°

The black body temperature of the tungsten lamp burning at an efficiency of one watt per candle was 2135° C. when measured with red light. When measured with blue light it was from 50° to 100° higher, varying with filaments from different sources. Hence the true temperature of the filament must at least be greater than 2200° C., since no body at a given temperature radiates more than a black body. We were finally led to assign 2300° C. as the approximate normal working temperature of the filament of the tungsten lamp burning at an efficiency of

one watt per candle. The very much higher working temperature of the tungsten filament, than the carbon, is therefore sufficient to account for a very considerable part of its increased efficiency. Selective radiation is also an important factor. If a carbon filament were burned at 2200°–2300°, its efficiency would be well within two watts per candle.

From the calibration equation of the filament, referred to above, giving the relation between the current through the filament and its black body temperature, it is possible to determine the melting point of the metal of which the filament is made by observing the current for which the filament melts, assuming that the above equation continues to hold good. In this way the melting points of tungsten and tantalum<sup>1</sup> were found to be 2890° and 2700° C. black body temperature (for red light), corresponding to true temperatures of about 3080° and 2900° respectively, the highest melting points ever observed. Wartenberg subsequently found by measurements with a Wanner pyrometer on a small lamp of tungsten at the instant of melting, which was accomplished by cathode ray bombardment in a vacuum tube, about 2800° C. for the black body temperature. He used  $c_2 = 14,600$  for the constant of the Wien equation. If his result is reduced to  $c_2 = 14,500$ , as used in the present investigation, his value would be some 25° higher, so that the results found by two such very different methods are in fairly satisfactory agreement for such very high temperatures.

*Heat Treatment of High Temperature Mercurial Thermometers.*<sup>2</sup>—The work of the testing developed the fact that a large percentage of the high temperature thermometers made in this country were subject to very considerable changes due to use at high temperatures, these changes amounting to 30° C. or more. This investigation was accordingly undertaken in order to direct the attention of American manufacturers to proper methods of annealing such thermometers.

When a thermometer, which has not been properly annealed, is exposed to high temperatures, the strains present in the glass are relieved to some extent, the glass contracts, and on cooling the ice point reading will have been raised. These changes of the ice point are much more rapid during the first few hours of heating, and become less as the time of heating is prolonged. The time required to reach an equilibrium condition is very long, as small changes of the ice point reading may still be detected after many hundred hours annealing. The results of annealing thermometers, made of different kinds of glass, at various temperatures, and for various long intervals of time are given in detail in this paper. The more important conclusions may be summarized as follows:

(1) Jena 59<sup>III</sup> borosilicate is one of the best thermometric glasses in use, particularly for high temperatures, but it cannot safely be used at much above 500° C.

(2) Jena 16<sup>III</sup> glass can be used up to 450° C. or somewhat higher with good results and for temperatures lower than 420° C. a softer glass may be used for the thermometer stem.

(3) Every thermometer, particularly if intended for use above 100° C., should undergo a suitable system of annealing or artificial aging before it is used. The annealing can be done before the thermometer is filled. Thorough annealing requires from four to ten days at about 450° C., according to the temperature at which the thermometer is to be used, and the annealing may well be followed by a period of slow cooling for from three to six days. (The latter is, however, less important.) The total change of the ice point for this process of annealing will be about 30° for Jena 16<sup>III</sup> glass and 20° to 30° for Jena 59<sup>III</sup> glass.

(4) The ice point of a thermometer will change with use

<sup>1</sup> C. W. Waidner and G. K. Burgess, "Des points de fusion du tantale, et du tungstène," *Bull. des Sciences de la Société Française de Physique*, 1907, pp. 200–204; *Jl. de Phys.*, 6, 830 (1907).

<sup>2</sup> H. C. Dickinson, *Bull. Bur. of Stand.*, 2, 189–223 (1906), reprint No. 32.

at the higher temperatures and must be determined occasionally if accurate results are to be had. If the thermometer has not been annealed at temperatures above 400°C. for 16<sup>III</sup> or 430°C. for 59<sup>III</sup> glass, the changes will be large if heated above the temperature at which it has been annealed. If changes have taken place in the ice point reading, the fundamental interval has probably changed (increased) by about 3 per cent. of this amount and the resulting error at 500° may be as much as one-fifth of the change of the ice point.

(5) To prevent boiling of the mercury in a thermometer the space above it should be filled with some dry, inert gas, such as nitrogen or carbon dioxide, having a pressure of one atmosphere at 300°, of four and one-half atmospheres at 450°, and of twenty atmospheres at 550°C.

(6) Care must be exercised that a thermometer is not overheated. If a long portion of the stem is cold the stem correction may amount to 30° or 40°C., and in this case the reading might be 500° when the temperature of the bulb was 540°C. and after a few minutes at that temperature the ice point might be 20° too low.

Since the completion of this work the Bureau has furnished the plans of the electric annealing furnace used in this work to a number of manufacturers, who have since installed similar furnaces, with the result that the thermometers now submitted for test are permanent in their indications.

*On the Standard Scale of Temperature in the Interval 0° to 100° C.*<sup>1</sup>—Not the least important of the many contributions of the International Bureau of Weights and Measures to the art of accurate measurement has been establishment of the International Hydrogen Scale of Temperature, as defined in the following resolution of the International Committee on Weights and Measures, adopted October 15, 1887:

"The International Committee on Weights and Measures adopts as the standard thermometric scale for the international service of weights and measures the centigrade scale of the hydrogen thermometer, having as fixed points the temperature of melting ice (0°) and the vapor of distilled water boiling (100°) at standard atmospheric pressure, the hydrogen being at an initial manometric pressure of one meter of mercury—that is to say,  $1000/760 = 1.3158$  times the standard atmospheric pressure."

The scale is preserved at the International Bureau by means of four primary standard mercurial thermometers which, after the most careful standardization, were directly compared by Chappuis with the hydrogen gas thermometer. Only a few years ago, before the introduction of the Hydrogen Scale, investigators were frequently compelled to spend more time in setting up a gas thermometer and establishing a temperature scale to which to refer their measurements than in the actual carrying out of the main objects of their investigation, with the resulting disadvantage that the relation between the temperature scales used by the different investigators was not accurately known.

Accordingly, the object of the present investigation was to establish a temperature scale which could be maintained and used with the highest attainable accuracy and which should at the same time be in agreement with the Hydrogen Scale, as defined and maintained at the International Bureau, to within the highest accuracy with which that scale is reproducible. For this purpose there were in possession of the Bureau of Standards 16 primary standard mercurial thermometers, all constructed of *verre dur* (French hard glass), the calibration corrections, pressure coefficients, and fundamental intervals of which had been determined at the International Bureau at various times from 1885 to 1903. Furthermore some of these standards had been directly compared with the fundamental

standards of that Bureau. These thermometers were made by Tonnelot and by Baudin, of Paris, and embody the highest perfection of workmanship. It could not be assumed that these thermometers, although made of the same kind of glass (*verre dur*), would define identically the same mercury-in-glass scale of temperature as the standard thermometers of the International Bureau, for not only does glass of the same trade name obtained at different times define slightly different temperature scales when made up into thermometers (the difference amounting to as much as 0.02° at 50° for *verre dur*), but even with thermometers made up from the same pot of glass there is quite an appreciable difference in their temperature scales, the slight difference in chemical composition and physical properties brought about in working the thermometer in the blast lamp being sufficient to cause such a difference. Hence, as the temperature scales defined by these thermometers would differ slightly from one another, one of the objects of this investigation was to determine the magnitude of these small differences; in other words, to determine the supercorrections that must be applied at different temperatures to the scale defined by each thermometer to reduce to temperatures on the mean scale of all the thermometers and then to determine the difference, if any, between this mean scale and the mean scale of the fundamental standards of the International Bureau from the supercorrections furnished by that Bureau for those thermometers that had been directly compared with their standards. For this purpose the calibration corrections, pressure coefficients, and fundamental intervals of all the thermometers were again redetermined with the greatest care and they were then intercompared in a specially designed thermometer comparator at every 10° in the interval 0° to 100°C. The results of this work, which included many thousands of observations, may be briefly summed up in the statement that the mean scale defined by these 16 primary standard mercurial thermometers is in agreement with the mean *verre dur* scale of the International Bureau and they serve to reproduce the International Hydrogen Scale to within the limits of accuracy at present attainable (about 0.002°) in mercurial thermometry.

*The Testing of Clinical Thermometers.*<sup>1</sup>—This paper contains the results of experiments and information having a direct bearing on the construction and testing of clinical thermometers such as discussion of types in use, scale of temperature on which they are graduated, the construction of suitable standards for use in pointing clinical thermometers, defects to which they are liable, change in reading with time, difference in reading when hot and when cold, etc.; also a description of the apparatus and methods used in testing, together with the regulations that have been adopted by the Bureau governing the testing and certification of clinical thermometers.

Tests of clinical thermometers found on the market, when this work was first taken up, showed that errors of 0.5° F. were quite common. Tests of groups of thermometers led to the conclusion that the standards used by the manufacturers were in error, a conclusion which was confirmed when these standards were submitted for test in reply to a circular letter addressed to the manufacturers. A number of specially designed and carefully calibrated standards were accordingly loaned by the Bureau to manufacturers, with a view to facilitating the use of standard thermometers of proper construction and the adoption of a uniform scale of temperature. The average errors of the thermometers now submitted for test are about one-third as large as they were a few years ago. In 1904 about 12% of the thermometers submitted failed to pass the test requirements, and previous to that date a much larger percentage. At the present time only about 5% fail.

The strains set up in glass in the process of working in the

<sup>1</sup> C. W. Waidner and H. C. Dickinson, *Bull. Bur. of Stand.*, **3**, 663-728 (1907), reprint No. 69.

<sup>1</sup> C. W. Waidner and L. A. Fischer, *Bull. Bur. of Stand.*, **1**, 275-289 (1904-5), reprint No. 13.

blowpipe are only relieved after a long period of time extending over many months and even years. The disappearance of these strains makes itself manifest by a slow contraction of the glass and a consequent rise in the reading of the thermometer. Hence, thermometers not aged, or "green" as they are called, might pass the most rigid test requirements, and yet, if made of certain kinds of glass, they might in the course of two or three months develop errors of  $0.6^{\circ}\text{F}$ . or more. In order to determine definitely the magnitude of the errors that might result from time changes, a series of experiments were undertaken with a large number of green clinical thermometers, made of different kinds of glass and by different manufacturers. The results of these experiments, based on many hundreds of observations, are given in the following table for different periods from the date the thermometers were made.

AVERAGE INCREASE IN READING OF CLINICAL THERMOMETERS.

Glass.	At end of 1 month	At end of 2 months	At end of 14 months.
Jena 16III glass . . .	$0.04^{\circ}\text{F}$ .	$0.06^{\circ}\text{F}$ .	$0.11^{\circ}\text{F}$ .
Soft glass. . . . .		$0.30^{\circ}\text{F}$ .	$0.68^{\circ}\text{F}$ .

These experiments show that if soft glass is used the time changes are by no means negligible. On the other hand, when the better grades of thermometer glass are used, such as Jena normal, Corning normal, or French hard glass, the total change in fourteen months is only about  $0.1^{\circ}\text{F}$ ., and about one-half of this total change takes place in the first two months. Other experiments have shown that time changes after fourteen months are insignificant. It is therefore evident that if clinical thermometers are made of the proper glass three or four months are sufficient to age them so that subsequent changes will be negligible.

The strains introduced in making the contraction or "trap" in the capillary stem of the thermometer, by which device the thermometer holds its highest reading until the mercury index is again thrown back, sometimes causes small slivers of glass to break off after long intervals of time, frequently rendering the thermometer untrustworthy. This defect is referred to because of the prevailing belief that if a thermometer has once been tested and has received a certificate, it will always remain reliable as long as it continues to register.

The so-called "time of action" of clinical thermometers, which so frequently gives rise to misunderstandings between the manufacturer and the user, depends largely on how the thermometer is used. Owing to the demand for short time of action the manufacturers have been compelled to use very small and thin wall bulbs and very fine capillaries, which results in a very frail thermometer and makes it difficult to throw back the index. To get the best results in use the thermometer should be kept under the tongue, and care should be taken not to inhale air through the mouth. The time of action varies from less than one-half minute to two minutes, or more for some of the larger types commonly used abroad. Many thermometers found on the market, marked "half-minute," require a much longer time to register within  $0.1^{\circ}$  of their final reading. In a water bath only 3 to 5 seconds are required for the thermometer to take up the temperature of the bath.

As a result of a large number of experiments on clinical thermometers found on the market, the following regulations governing their test were adopted by the Bureau.

Before being tested for accuracy clinical thermometers are examined for defects of construction, such as presence of air bubbles or moisture in the mercury or in the capillary bore, cracks in the glass and defective graduations; the operation of the registering device ("index") is also tested to see that the index is neither too easy nor too difficult to throw back. When large numbers of thermometers have to be tested, the usual method of throwing back the index by hand is impracticable, on account of the time and effort required. This test is ac-

cordingly carried out by mounting a large number of the thermometers in a whirling machine with the bulbs turned away and at a definite distance from the axis, in which position they are rotated at a definite predetermined speed; all thermometers that hold their index in this test are rejected as presenting too much difficulty in throwing back the index in ordinary use. If this test is passed the thermometers are then compared in an electrically heated and motor-stirred water bath with two standard thermometers of the Bureau at the four test points,  $98^{\circ}$ ,  $100^{\circ}$ ,  $104^{\circ}$  and  $108^{\circ}\text{F}$ ., two independent comparisons being made at each point. If the two tests at any point differ by more than  $0.15^{\circ}\text{F}$ ., or if the mean of the two tests gives a correction in excess of  $0.3^{\circ}\text{F}$ ., the thermometer is rejected. Furthermore, errors in the value of an interval between test points must not exceed  $0.3^{\circ}\text{F}$ .

*Calorimetric Resistance Thermometers.*<sup>1</sup>—The highest accuracy attainable with even a most carefully standardized calorimetric or Beckmann thermometer, graduated to  $0.01^{\circ}$ , is hardly as good as  $0.002^{\circ}$ . On account of the large and variable capillary forces due to the meniscus, the accuracy cannot be further increased by lengthening the scale degree, as this would require either a larger bulb, thus increasing the lag of the thermometer, or a smaller capillary bore, which would increase the variable effects of these forces.

To meet the requirements of calorimetric measurements of the highest accuracy, some platinum resistance thermometers were constructed which were especially adapted to the measurement of the small temperature differences of  $2^{\circ}$  or  $3^{\circ}\text{met}$  with in such work, to an order of accuracy of 2 or 3 parts in 10,000, and which at the same time had so small a lag that when suddenly plunged into an ice or steam bath they would assume the temperature of the bath to within  $0.001^{\circ}$  in a few seconds. The thermometers were made with four leads of thin copper about 4 mm. wide and 0.12 mm. thick, separated by thin strips of mica. To the ends of two of the leads was fused the platinum coil, consisting of about 10 cm. of 0.02 mm. wire wound as a flat coil on a mica strip, and having a resistance of about 30 ohms in ice and 40 ohms in steam. The other two leads known as the compensating leads were joined together at the lower ends by a short strip of platinum wire. When these leads are put into the arm of the Wheatstone bridge adjacent to the arm in which the coil is found, the thermometer is compensated for a variable depth of immersion. The leads and coil were then covered on each side with thin strips of mica and the whole enclosed in a thin and close-fitting copper sheath, about 7 mm. wide and 1 mm. thick. The hard rubber or glass head of the thermometer, where the four copper leads are soldered to the four silk insulated stranded copper leads used to connect the thermometer to the bridge, was hermetically sealed after partly filling with phosphorus pentoxide to keep the interior of the thermometer perfectly dry and thus to maintain a high insulation resistance between the two pairs of leads. When so constructed the lag of these thermometers behind the temperature of a bath whose temperature was varying was so small that it could not be measured with any degree of certainty, being certainly much more than 100 times less than the time constant of a Beckmann thermometer, so that the error in the measurement of small temperature intervals with these thermometers, due to lag, is absolutely negligible in the most refined calorimetric work.

These thermometers were used in connection with a specially designed Wheatstone bridge capable of rapid setting to the nearest  $0.00001$  ohm, corresponding to  $0.0001^{\circ}$ . They were calibrated by intercomparisons at  $30^{\circ}$ ,  $40^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$  and  $70^{\circ}\text{C}$ . with eight of the primary standard mercurial thermometers previously described.

<sup>1</sup> H. C. Dickinson and E. F. Mueller, *Bull. Bur. of Stand.* **3**, 641-661 (1907), reprint No. 68.



*The Transition Temperature of Sodium Sulphate.*—For the complete standardization of a platinum resistance thermometer, only one other temperature is needed in addition to the two temperatures of ice and steam. The above carefully standardized calorimetric resistance thermometers were accordingly applied to the determination of the transition temperature of sodium sulphate with a view to the redetermination of this fixed point with the highest attainable accuracy so that it might in the future serve as the third fixed point for the standardization of calorimetric thermometers intended for work of high precision. This investigation showed that, starting with the "Kahlbaum" sodium sulphate or with the sulphate obtained by neutralizing the carbonate, it was possible by a few recrystallizations to obtain the material in such a state of purity that it would give a fixed point that was sharp and definite to  $0.001^\circ$ . The transition temperature of the purest product was found to be  $32.384^\circ\text{C}$ . on the International Hydrogen Scale of Temperature, in most excellent agreement with the determinations of Richards and Wells, who found  $32.383$ , using mercurial thermometers standardized at the International Bureau of Weights and Measures. For "Kahlbaum" sodium sulphate as supplied, the transition temperature was found to be  $0.004^\circ$  lower than for the purest samples.

If in the standardization of a platinum thermometer the true transition temperature of the sodium sulphate used should differ by  $0.01^\circ$  from the assumed value, the resulting error in the value of the constant,  $\delta$  (see below), of the platinum thermometer would be about 3 per cent. While this would introduce an error of about  $0.007^\circ$  in the absolute value of the temperature at  $20^\circ$ , the error in a small temperature interval in calorimetric work at the latter temperature would be less than 1 part in 3000. For a small temperature interval in the neighborhood of  $50^\circ$ , the resulting error would be practically zero, and in the neighborhood of  $0^\circ$  about 1 part in 2200.

Resistance thermometers standardized in ice, steam and sodium sulphate purified by several recrystallizations, will serve to reproduce the International Hydrogen Scale of Temperature to the highest accuracy within which that scale is fixed and reproducible (about  $0.002^\circ$ ), and thermometers so standardized may be used for the measurement of the small temperature changes met with in calorimetric work with an accuracy satisfying every present requirement.

*The Specific Heats of Brines.*<sup>1</sup>—The determination of the specific heats of calcium chloride brines, undertaken at the request of the refrigeration industries, was completed during the present year. Preliminary results were communicated to the International Congress on Refrigeration held at Paris in 1908. Commercial brines of very different chemical composition as well as brine from chemically pure  $\text{CaCl}_2$  were included in this work. Two entirely different types of calorimeters, (a) the constant flow calorimeter and (b) the Dewar vacuum flask calorimeter, were used. The results by the two methods are in excellent agreement.

In the first method the calorimeter was suspended within an enclosure, the metallic walls of which were kept at a constant temperature. A steady stream of cold brine was kept flowing through a copper worm in the calorimeter, the worm being immersed in the stirred oil with which the calorimeter was filled. The calorimeter was constantly kept at the same temperature as the surrounding walls of the enclosure by suitable regulation of the electrical energy supplied to a heating coil wound around the copper worm in the calorimeter. This was effected by the use of a differential copper-constantan thermocouple with one junction in the calorimeter and the other junction in contact with the walls of the enclosure and a delicate rheostat for regulating the supply of electrical energy. Under

these circumstances the calorimeter loses no heat to the surroundings, the so-called "cooling correction" of the calorimeter is entirely eliminated, and all the electrical energy supplied goes to raising the temperature of the brine. The difference in temperature between ingoing and outgoing brine was measured by two calorimetric platinum resistance thermometers previously described, so that from the amount of brine flowing through the calorimeter in a given time and the amount of electrical energy supplied for heating the brine, the necessary data were at hand for computing the specific heat of the brine.

In the second method, a weighed amount of the cold brine was put into a Dewar flask, the space between the double glass walls of which was highly evacuated so that the loss of heat from the inner vessel, in which the brine was placed, was very small. The brine had been previously cooled to the desired low temperature at which measurements were to begin by circulating a cold stream of  $\text{CO}_2$  gas, obtained by allowing the gas to expand through a suitable valve, through a copper worm immersed in the brine. The rise of temperature caused by an accurately measured amount of electrical energy supplied to a well-insulated constantan heating coil immersed in the brine was measured with a platinum resistance thermometer. The very small radiation correction, as well as the water equivalent of the inner wall of the flask and the energy supplied by stirring, was accurately determined. The results of determinations by this method on brine from chemically pure calcium chloride of densities 1.14, 1.20 and 1.26 are given in the following table:

SPECIFIC HEAT OF C. P.  $\text{CaCl}_2$  BRINE.

Temp °C	1.140	Densities 1.200	1.260
-25			0.647
-20		0.695	0.651
-15	0.764	0.700	0.654
-10	0.768	0.705	0.657
-5	0.772	0.709	0.660
0	0.775	0.712	0.663
+5	0.778	0.715	0.666
+10	0.781	0.719	0.670
+15	0.784	0.722	0.673
+20	0.787	0.725	0.676

At  $0^\circ$  the relation between the specific heat,  $\sigma$ , and the density,  $\delta$ , may be represented, to within 0.1% by the following equation:

$$\delta = 2.6054 - 3.0169\sigma + 1.3515\sigma^2$$

the slope of this curve  $d\delta/d\sigma = 3.0169 + 2.7030\sigma$  may be used for interpolation between values given in the above table (putting  $\sigma$  = the mean of the given and interpolated specific heats). Above  $0^\circ\text{C}$ . the interpolation will be good to 0.1% and below  $0^\circ\text{C}$ . the error will not exceed 0.4% at the lowest temperature.

In addition to the chemically pure brine, four commercial calcium chloride brines were included in these experiments, ranging from almost chemically pure to a brine containing over 30% of magnesium chloride, the corresponding range of specific heats at  $0^\circ$  being only from 0.2% higher to 0.4% lower than for the chemically pure brine. At low temperatures the specific heats were the same to within 0.2%.

The first method described above, which was used with only one of the commercial samples, gave results agreeing with the above to within 0.3%.

*Standardized Heat Samples.*—In response to numerous requests from chemists and engineers, the Bureau has furnished a considerable number of standard heat samples of known calorific value for the standardization of combustion calorimeters. In consequence of the growing practice of awarding large contracts for fuels on the results of determinations by combustion calorimeters, the preparation of these standard heat samples and the standardization of the finely graduated thermometers used in the tests, have already done much to increase their accuracy and to bring them to a uniform basis. Thus far, this work has been confined to furnishing analyzed samples

<sup>1</sup> H. C. Dickinson, E. F. Mueller and E. B. George *Bull. Bur. of Stand.*, reprint No. 135.



of cane sugar of the highest purity. Work is, however, under way on the determination of the heats of combustion of other substances, such as benzoic acid, naphthalene, anthracene, hippuric acid, etc. By thus enabling chemists and engineers to test the accuracy of their apparatus and methods, the Bureau is relieved of the necessity of doing a large amount of routine testing, which can very well be taken care of by private laboratories, while at the same time accomplishing the important end in view, *viz.*, the use of standardized apparatus and methods which will enable different observers to obtain strictly comparable results. The meaning of "accuracy" is well illustrated by the statement of one firm writing to the Bureau concerning the test of the calorimetric thermometer used by them in the determination of the heat values of coals; a difference of only six one-hundredths of a degree had developed between the standard thermometer of this firm and the standard used by one of their customers, yet this difference amounted to \$15,000 per year.

*Thermodynamic Scale of Temperature.*<sup>1</sup>—It is desirable for many purposes and essential to precise scientific work that measurements of temperature should be expressed in or be reducible to some one standard scale. The thermodynamic scale, or scale of the ideal gas thermometer, is generally agreed on as the best for this purpose. Practical gas-thermometer scales differ from this by various small amounts. These differences, *i. e.*, the corrections to be applied to the actual gas scales to reduce them to the thermodynamic scale, must be determined from the thermometric gases, since the ideal gas does not itself exist.

The best data available have been utilized in a recomputation of these corrections for nitrogen, and the results compared with recent work by other methods, the agreement being well within the present limits of accuracy in gas thermometry. The most probable values of the corrections of the nitrogen scale as deduced from this computation together with recent work by D. Berthelot and Callendar are given for a few points in the following table:

Temperature °C.	50°	200°	400°	600°	1000°
Constant pressure.....	-0.02	+0.12	-0.49	-0.92	-1.95
Constant volume.....	-0.01	+0.04	-0.16	-0.32	+0.72

These values are applicable when the constant pressure, or when the initial pressure at the ice point, is one meter of mercury. For other pressures the corrections are nearly proportional to these pressures.

The corrections of the hydrogen scale appears to be within the experimental errors at present unavoidable in gas thermometry, at all temperatures above the ice point.

Further work on the properties of the thermometric gases is needed and some of it is in progress in various laboratories both in this country and abroad. An extended experimental investigation of the Joule-Thomson effect is in preparation, the results of which will be used in a revision of the computations and will permit of greater certainty in the resulting corrections of the usual gas scales. This work will also have a direct bearing on problems connected with the liquefaction of gases.

*The Action of the Hampson Liquefier.*<sup>2</sup>—This machine is in common use for liquefying air, and to some extent for hydrogen, and it seemed desirable to make a more complete theoretical study of the process involved than has heretofore been published, as an aid in clarifying our ideas on the mode of operation and, if possible, suggesting improvements in design or efficiency of working. It was found that the theory could be put into quite simple form and that data were available which permitted a comparison with published results on the liquefaction of air by such machines. The adequacy of the theory was shown by the agreement thus obtained.

The total cold available per unit mass of gas fed into the liquefier depends solely on the pressure and temperature of the gas. The regenerator coil should have surface enough to bring the exhaust sensibly to the feed temperature; otherwise the remaining difference represents a loss of cold and a proportional waste of liquid that might have been obtained. Any heat that leaks into the liquefier *anywhere*, also represents a loss of cold and a proportional waste of liquid. The particular arrangement of the regenerator coils and the design of the valve have no influence on the fraction of the gas liquefied except as they may indirectly influence the temperature distribution in the liquefier and hence the thermal leakage through the insulation. These statements refer only to the steady state and not to the starting period, the duration of which may be considerably influenced by the design of the liquefier.

The cooling effect and the fractional yield can not be increased indefinitely by raising the initial pressure. When the air fed in is cooled by ordinary tap water, the fraction liquefied under the best possible conditions of insulation with pressures of 80, 130 and 200 atmospheres, are about 4, 6½ and 8¼%; and the maximum attainable by further increasing the pressure is probably not over 12 per cent. which would be reached in the vicinity of 400 atmospheres.

At a given temperature and rate of feed, the waste due to imperfect insulation is nearly constant and independent of the initial pressure, so that it is relatively more important at low pressures, which are therefore not economical.

Artificial precooling increases the fraction that it is possible to liquefy. At 130 atmospheres and initial temperatures of +16°C., -35°C. and -78°C., the maximum percentages of the air fed in that could be liquefied under the best conditions, are about 6½, 9 and 14 per cent., respectively.

The substitution of a motor for the expansion valve permits of taking energy from the gas in the form of mechanical work, which is equivalent to an additional source of cold beyond that furnished by the Joule-Thomson effect in expansion through a throttling valve. Computations have been made regarding the advantage to be gained by adopting the familiar suggestion of substituting a turbine for the expansion valve, and designs for such a liquefier, to be built for experimental purposes, have been partially completed.

*On Methods of Obtaining Cooling Curves.*<sup>1</sup>—When physical or chemical transformations take place in matter, such changes are usually accompanied by the absorption or evolution of heat. The temperatures, called "critical points," at which such changes take place are most conveniently determined from the discontinuities in the "cooling" or "heating curves" taken by means of a thermocouple or other suitable pyrometer, while the substance is cooled or heated. The determination of the critical points of steels is a very important problem in metallurgy, inasmuch as variations of 25°C., or thereabouts, in the relation of the critical point of some steels to the temperature at which they are hardened has a very marked effect on the structure and physical properties of the steels. In this paper the various methods of taking cooling curves are discussed at length together with the characteristics of various types of these curves and the interpretation of data so obtained. The various kinds of apparatus used in thermal analysis are briefly described and some modifications in methods and apparatus are suggested, some of which have been used in our laboratories with satisfactory results.

*Platinum Resistance Thermometry at High Temperatures.*<sup>2</sup>—The measurement of temperatures based on the change in the electrical resistance of a platinum wire (and other metals at comparatively low temperatures) is finding wide application,

<sup>1</sup> E. Buckingham, *Bull. Bur. of Stands.*, **3**, 237-293 (1907), reprint No. 57.

<sup>2</sup> E. Buckingham, *Bull. Bur. of Stands.*, **6** (1909), reprint No. 123.

<sup>1</sup> G. K. Burgess, *Bull. Bur. of Stands.*, **5**, 199-225 (1908-9), reprint No. 99.

<sup>2</sup> C. W. Wadner and G. K. Burgess, *Bull. Bur. of Stands.*, **6** (1909), reprint No. 124.

especially in the measurement of ordinary temperatures from some central location and for the medium range of high temperatures up to about 1000° C. For laboratory uses, the resistance thermometer is peculiarly adapted to the measurement of small temperature intervals with the highest attainable accuracy, *e. g.*, in calorimetry, and for work in the interval from the temperature of liquid air or lower up to about 800° C. it affords the most precise measurement of temperature at present available. At higher temperatures it is subject to slight changes during use, so that the platinum thermocouples become more convenient to use, being much less subject to such changes. The present investigation was undertaken to determine with what accuracy Callendar's formula could be applied in the calibration of platinum thermometers in the range 0° to 1100° C., and how much the temperature scales of these thermometers calibrated on the basis of this formula, would differ when the thermometers were made of platinum of different degrees of purity.

Temperatures on the platinum scale are numerically defined in terms of the resistance of the platinum coil of the thermometer, as follows:

$$pt = 100(R - R_0) / (R_{100} - R_0)$$

and the difference between the platinum scale, so defined, and the gas scale of temperature is given by the Callendar formula:

$$t - pt = \delta \left( \frac{t}{100} - 1 \right) t$$

$R$  is the observed resistance at the temperature,  $t$ , and  $R_0$  and  $R_{100}$  are the resistances at 0° and 100°, respectively. The fundamental interval  $F$ ,  $F = R_{100} - R_0$ , and the fundamental coefficient  $c = (R_{100} - R_0) / 100R_0$ . The constants  $\delta$  and  $c$  are characteristic of the material of the thermometer. For platinum of the highest purity  $c = 0.0039$  about and  $\delta = 1.50$ . For impure platinum  $\delta$  is larger and  $c$  is smaller than for pure platinum. This affords probably the most delicate known test of purity.

Nine platinum thermometers were used of wire varying in diameter from 0.05 to 0.6 mm. and having a range of  $R_0$  from 0.11 to 21.3 ohms, of  $c$  from 0.0039 to 0.0017, and of  $\delta$  from

1.50 to 1.80. The thermometers were of the compensated lead and of the potential terminal types. Measurements with the former were taken by means of a special Wheatstone bridge and with the latter by a potentiometer method. The resistance measurements were accurate to 1 or 2 parts in 100,000. After the construction of the thermometers, and before use, they were annealed for several hours at about 1100° C.

As will be seen from the above equations, observations of the resistances at three known temperatures are sufficient to determine  $\delta$ , and thus completely standardize a platinum thermometer. Two of these temperatures are those of melting ice (0°) and of steam (100°) at standard atmospheric pressure (760 mm.). The third temperature usually used is the boiling point of sulphur (444.70°) at standard pressure. In this connection all the necessary precautions were investigated to insure that the vapor of boiling sulphur shall give a definite temperature accurately reproducible to a few hundredths of a degree. The thermometers, thus standardized by observations in ice, steam and sulphur vapor, were applied to the determination of the freezing (or melting) points of tin, cadmium, lead, zinc, antimony, aluminium, silver, pure copper, copper saturated with cuprous oxide, and the eutectic alloy of silver and copper (72Ag-28Cu). Samples of these metals obtained from various chemical firms and furnished as C. P. were used, so that data which were obtained on the accuracy with these metals can be used to give fixed temperatures for the standardization of pyrometers. To prevent oxidation the metals were used in crucibles of pure graphite, with powdered graphite covering them, and in amounts of 1.5 to 2 kilograms, thus ensuring ample depth of immersion of the coil of the thermometer. The melting and freezing point determinations were carried out in vertical electric resistance furnaces wound with two platinum ribbon heating coils on concentric porcelain tubes, the winding being so spaced as to give quite uniform temperature distribution throughout a considerable length of the furnaces. The temperature could be maintained constant to within a few hundredths of a degree for many minutes during the freezing or melting of the metal. By stirring with the thermometers, undercooling could be almost entirely avoided with most of the metals (except antimony). The temperatures found for the freezing and the melting point,

SCALE OF PLATINUM THERMOMETER. CALLENDAR FORMULA.

Metal	Temp. °C.	Range deg. C.	Number of		
			Obs.	Samples	Thermoms.
Sn.....	231.92	0.04	4	1 K	2
	231.89	0.09	6	3	2
Cd.....	321.01	0.09	3	K	2
Pb.....	327.88	0.01	2	1	1
		0.04 <sup>a</sup>	6	K	1
Zn.....	419.37	0.11	9	3	1
		$\delta = 1.516$			
	419.30	0.06	5	K	1
Sb.....	630.71	0.57	3	K	2
Melting point	630.80	0.15	4	2 K	1
Ag-Cu	779.55	0.08	3	1	2
71-29					
Ag-Cu	779.18	0.45	6	1	3
72-28					
Ag-Cu	779.23	0.30	3	1	2
73-27					
Ag.....	960.88	0.10	8	1	3
Cu.....	1083.04	1.61	7	B. C. W.	3
	1082.88	2.26	13	4	4

<sup>a</sup>Range" = difference between highest and lowest F. P. determinations.

<sup>b</sup>Number of samples" refers to materials from different chemical firms.

<sup>c</sup>"K" = "Kahlbaum" "B. C. W." = Baltimore Copper Works' purest product.

CALIBRATION DATA. ICE, STEAM, SULPHUR. °S = 444.70° C.

Temp. °C.	Range deg. C.	Number of			Temp. °C.	Range deg. C.	No. of obs.	Gas scale, H <sub>2</sub> born and Day
		Obs.	Samples	Thermoms.				
157.0	0.002 to 214				1203	0.0017		
231.82	0.08 <sup>a</sup>	4	3	1				
320.95	0.02	2	1	1				
419.32	0.08	8	3 K	1				
	0.16	11	5	1				
419.28	$\delta = 1.551$							
		1	K	1				
631.25	0.17	4	3 K	1	632.65	0.09	2	630.6
631.06	0.08	3	3 K	1				
781.21	0.06	2	1	1				
966.21	0.02	2	1	1	975.28	0.08	2	961.5
1091.92	1.15	4	3	1	1106.2		1	1084.1

respectively, were practically identical when the cooling or heating was sufficiently slow. The results of the freezing-point determinations are summarized in the accompanying table.

It will be seen that for thermometers of pure platinum, for which  $\delta = 1.50$ , calibrated on the basis of the Callendar equation, by observations in ice, steam, and sulphur, the temperature scale thus defined up to at least  $1100^{\circ}\text{C}$ . is in agreement with the generally accepted gas scale to well within the limits of accuracy with which that scale is known at the present time. For thermometers of impure platinum, it will be seen, that this equation no longer holds. A modified method of calibration, applicable to impure platinum, is discussed at length in the full paper, in which one other calibration temperature is used, such as the F. P. of Ag or of Cu, and in which  $\delta$  is not taken as a constant but as having different values ( $\delta = a + bt$ ) at different temperatures.

Thermometers of the purest obtainable palladium wire were also tried, for which  $\delta = 2.89$  and  $c = 0.00336$ . They do not satisfy the Callendar equation; for example, it leads to a value of  $1152^{\circ}\text{C}$ ., for the F. P. of copper; up to  $600^{\circ}\text{C}$ ., however, the equation holds within  $1^{\circ}$ .

The effects of high temperatures on the constants of platinum thermometers is, in general, to reduce the value of  $R_0$  and increase F. I., *i. e.*, the effect is as if the platinum were purified by the loss by evaporation of impurities, such as iridium. When the wire is very pure to begin with  $R_0$  generally increases slightly and  $c$  decreases, due to the combined effects of strains caused by thickening of the mica frame and of contamination of the wire. The changes are much less for pure than for impure platinum. With thermometers of pure platinum and not too fine wire, wound on the mica frame as free from strains as possible, the changes in  $R_0$  after some ten determinations of the freezing points of silver and copper (corresponding to about 25 hours use) were only a few tenths of a degree. For about equal use, one of the thermometers of impure platinum ( $\delta = 1.57$ ) and very fine wire (0.05 mm.) showed a decrease of  $R_0$  corresponding to  $6.5^{\circ}$ . Thermometers of pure platinum and heavy wire (0.6 mm.) without the usual mica supporting frame showed unusually small changes in  $R_0$  even after several heatings for some hours each at  $1250^{\circ}\text{C}$ ., changes equivalent to only a few tenths of a degree.

The freezing point of the silver-copper eutectic ( $779.2^{\circ}$ ) is a convenient fixed point in the long interval of over  $300^{\circ}$  between the freezing points of antimony and silver.

Pt, Pt-Rh and Pt, Pt-Ir thermocouples, calibrated in terms of the equation  $e = a + bt + ct^2$  at three of the freezing points as found with thermometers of pure platinum (*e. g.*, Zn, Sb, Cu or Zn, Ag-Cu, Cu), were found to be in agreement with one another and with the scale of the platinum thermometer at intermediate temperatures to within  $0.3^{\circ}$ .

*Work under Way.*—In addition to the work now under way which has already been referred to, encouraging progress has been made in the following investigations:

(a) The determination of the heats of combustion of industrially important gases, using several different bomb calorimeters, different methods of calorimetry, calorimetric platinum resistance thermometers, and electrical standardization of bombs. The work was undertaken in order that the Bureau might prepare standard tables of the calorific values of gases for the use of the gas industries. In this investigation will also be included an examination of the leading types of gas calorimeters used in the industries in this country and abroad, with a view to determining the order of accuracy attainable with the various instruments, their limitations, and the precautions that must be observed in their use under various conditions.

(b) An intercomparison of the various viscosimeters used

in this country and abroad for the examination of the viscosities of oils, and their comparison with absolute viscosimeters, to enable engineers to intercompare results found with different instruments. This work was undertaken to assist the International Petroleum Congress and the various engineering societies who are endeavoring to bring about some uniformity and some improvement in the present unsatisfactory status of oil testing.

(c) The determination of the emissivities of substances at high temperatures, to which optical pyrometers are being applied in the industries (*e. g.*, steels, bronzes, etc., in both molten and solid conditions, carbon, porcelain, glass, etc.), with a view to determining the departure of the radiation from these substances from black body radiation and thus to enable the necessary corrections to be applied to the indications of optical and total radiation pyrometers to get the true temperature of the material under observation.

(d) The determination of the melting points of the highly refractory elements and materials, for which little or no data are at present available.

(e) The intercomparison of the temperature scales defined by the Wien-Planck and Stefan-Boltzmann radiation laws up to the highest attainable temperature. This work must serve for the establishment of the high temperature scale above the range of the gas thermometer.

(f) The establishment of the temperature scale in the interval  $100^{\circ}$  to  $500^{\circ}\text{C}$ . with the highest accuracy, in a way very similar to that already described for the standard scale in the interval  $0^{\circ}$  to  $100^{\circ}\text{C}$ .

*Circulars of Information.*—Two circulars have thus far been issued by the Heat Division, *viz.*:

No. 7. Pyrometer Testing and Heat Measurements (2nd edition).

No. 8. Testing of Thermometers.

Circular No. 7 contains information relating to the high temperature scale, the methods of standardizing and important precautions that should be observed in the use of thermoelectric, electrical resistance, optical and radiation pyrometers, the various heat tests the Bureau is prepared to undertake, and tables of fees charged for testing.

Circular No. 8 contains information relating to the thermal properties of glasses, the fundamental principles of mercurial thermometry, the construction and methods of use of thermometers, low temperature thermometers, and tables of fees for testing thermometers.

A circular containing complete specifications for a set of high-grade mercurial thermometers, suitable for laboratory standards, for measurements in the interval  $-35^{\circ}$  to  $525^{\circ}\text{C}$ ., is in preparation.

*Furnishing Information.*—One of the functions of the Bureau is to furnish to engineers and technical men such information as may be in our possession, relating to physical constants, the properties of materials, methods of measurements, etc. To this end correspondence is invited. Our laboratories are always open to those interested in the various lines of work in progress or in search of such information as we may have and which might be of assistance in promoting the application of scientific methods in the industries.

## ADDRESSES.

### THE CHEMIST'S PLACE IN INDUSTRY.

By ARTHUR D. LITTLE

Chairman Division of Industrial Chemists and Chemical Engineers.

The industrial chemist who believes that "life is not made for science but science for the development of life" takes no narrow view of what life is or what its best development must



mean. He recognizes that there is a hunger of the mind and a hunger of the spirit no less than a hunger of the body, and that only in such measure as all are satisfied does life become worth living and result in growth. He is therefore quick to render full meed of honor and appreciation to those workers in his own or other branches of science who pursue the truth for the truth's sake. He believes with them that the truth alone shall make us free. He resents however and denies the imputation that he is any less valiant for the truth than they, merely because the particular truth he seeks is one which has an obvious and immediate application to "the development of life." Especially does he repudiate the pedantry which as Thomson puts it "would regard science as a 'preserve' for intellectual sportsmen."

The industrial chemist asks no better definition of science than that contained in Huxley's famous dictum: "Science is organized common sense," and he believes with Sir Michael Foster that "Men of science are common men drilled in common sense." Where then shall common sense find better field for exercise and adequate expression than in those industrial activities on which our daily life depends? To this field then the industrial chemist devotes himself without apology, being well aware that before the hunger of the spirit or the hunger of the mind can be appeased, the hunger of the bodies moving by millions through the world must first be satisfied.

In its effort to satisfy this hunger modern industry has developed a complexity of organization, a magnitude of operation, a scale of expenditure and a drive and pressure of production far beyond anything which the world has seen before. Men and machines have alike been speeded up, worn out and cast aside. The march of progress has been over a continuous battlefield upon which the old was ever struggling with the new, new methods of organization, new principles of practice, new processes of production, new conditions of supply, new relations between man and his work. Accompanying it all in our own country at least has been a riot of waste lighting up the background with the flame from forest fires, burning oil wells, wasted gas and beehive coke ovens; cumbering the field with forest litter, piles of culm and slag, scrapped machinery and abandoned plant; poisoning our water courses with wastes which bore away a profit. With us through all our recent industrial development the watchword has been "increased production." To that we have sacrificed our resources, our future and the well-rounded development of our own lives. Our reward, inadequate though it is, has come in a producing capacity beyond all precedent and in costs of production so low as to be ruinous if continued long enough. We have succeeded because of a supply which once seemed limitless of the cheapest raw material the world has known. The conditions and practice of the past may serve for the development and exploitation of a new country but they involve wastes so stupendous as to spell bankruptcy for that country at maturity unless changed.

Evidence is everywhere at hand that the day of cheap raw material is passing if indeed it is not already past. To those who read the signs the watchword of the future is even now clearly outlined; it is no longer "increased production" but "increased efficiency in production."

It is into a world thus constituted that the chemist who elects to apply the organized common sense of science to industrial problems finds himself projected. It is a world in which great and avoidable wastes are everywhere existent, but a world which nevertheless is fostering and encouraging a growing sentiment for conservation. It is a world, used to progress at any cost, awakening to the value of the scientific method as an aid to progress and already under a heavy burden of obligation to chemistry for the achievements of the past. Into this world he comes with his activities still unfortunately shaded in many minds by the penumbra of the mystery which surrounded the old alchemists. Small wonder that he insists that the science

to which he owns allegiance is nothing more than organized common sense, the common sense which would check waste, increase efficiency, get the utmost possible return from all expenditure whether of capital, material or effort.

In justification of his claim to capacity in practical affairs the chemist can point to a brilliant record of accomplishment—a record of colossal industries which had their small beginnings in his laboratory, of waste places made to blossom, of mountains of discarded refuse turned to profitable uses, of industrial revolutions initiated by him, even a record of prestige and power brought to nations by his discoveries. Nevertheless it remains true, as the chemist himself will be the first to acknowledge that the results accomplished in the past have in large measure been independent of his training and that in his relation to present-day industry he is handicapped in many ways. At the outset of his career he is confronted with such multiplicity of detail in the province of knowledge he has chosen for his own as to leave little time for the studies and accomplishments which make for breadth of culture and a wide outlook upon life. He is taught to deal with things only to find that progress is often determined by an ability to deal with men. He spends years in acquiring the difficult technique of chemical analysis and when facility is at last attained, sometimes forgets that analysis is after all only a means of securing data upon which to base subsequent action and that chemists who make it an end soon reach that end and stay there. His work is confining. It is largely carried forward in the seclusion of the laboratory and often under conditions which impose secrecy. It is not then surprising if through lack of opportunity the chemist sometimes fails to acquire that knowledge of affairs which is an essential prerequisite for any commanding influence and without which the difficulties of taking one's proper place in the world of men are enormously enhanced. Moreover, as the result of industrial conditions, the limitations of his training, and his own lack of capital, the chemist who devotes himself to applied science almost invariably does so as an employee. He is apt through want of initiative or under the compelling force of circumstance to remain an employee, whereas he should far more often seek out and utilize the opportunity of directing capital along lines of independent enterprise. Most of all, perhaps, the industrial chemist of the past has been handicapped by the limitations of his knowledge, by his inability to translate the findings of the laboratory into terms of actual practice. He has been content too often to merely take the pulse and temperature of the patient and leave to others the diagnosis and the cure. Particularly has the industrial chemist been weak upon the engineering side, in the adaptation of means and ends upon the large commercial scale.

For these reasons and to this extent he has failed and often still is failing to "deliver the goods." His failure reacts directly upon himself and indirectly upon the whole profession. The making of chemical analyses is ceasing to involve the exercise of a profession. It has almost become a trade. In Pittsburgh Hungarian boys whose normal earning power is \$7.00 a week, are quickly trained to make from twenty to thirty silicon determinations a day. Flue gases are now analyzed every ten minutes and the results plotted in a curve by ingenious and accurate machines.

Some chemists see in these developments of the purely manipulative side of chemical work the beginning of the end for the profession. Nothing could be further from the truth. When Hungarian boys make silicon determinations and machines record the carbonic acid content of flue gas, the chemist who is worthy of the name is not displaced, he is set free, free to devote himself to larger problems and equipped with more comprehensive data for their attack. Let us then while fully recognizing the dignity of analytical work, never forget that it is after all only a means to an end, and that it derives its dignity from



the use to which it is put. There is no dignity in analyzing a water sample brought in by somebody in a four-ounce bottle smelling strongly of vanilla.

That the conditions of which some complain have long been impending is proved by the fact that twenty years and more ago no less a chemist than Sir William Crookes felt himself impelled to publish in the columns of *The Chemical News* frequent warnings to students in chemistry in which he pointed out the lack of recognition and the meager monetary rewards awaiting them. He specifically and with dire emphasis refers to one gentleman behind whose name trailed the letters M.A., F.C.S., F.I.C., who was called upon to determine from April to November, both inclusive, butter fat and total solids in thirty-six samples a week for a total honorarium, it could hardly be called a payment, of £20 or something less than 4d. a sample. One ought to be sorry for the gentleman and appalled at the decadence of British science, but somehow one cannot help feeling that the man who made the analyses at such a price received all the work was worth and that if he and others in his case had busied themselves about more important matters the outlook for chemistry in England would have been more encouraging.

But this is enough and more than enough of the pessimistic view of the chemist's place in industry. Let us turn to a consideration of the opportunity which really lies before him.

The first object of the industrial chemist should be that of increasing industrial efficiency. What are the factors upon which industrial efficiency depends, and to what extent can he hope to influence them? The principal factors are:

- Cheap raw material.
- Cheap power.
- Efficient labor.
- The control of processes.
- The elimination of wastes.
- The maintenance of standard in product.
- Cheap transportation

To an audience of chemists it is only necessary to state these factors in order to indicate at once the commanding influence which members of our profession should exert in case of each of them. That we have sometimes failed to make this influence felt, has been from other causes than lack of opportunity. A brief analysis must make this clear.

It is within the power of the chemist to determine the selection of the most efficient and therefore the cheapest raw material, to control the quality of that material in many instances through specifications, inspections, analyses and physical tests, to open up new sources of supply for the same or an alternative material. In the present state of industry it is easily possible for the chemist to institute savings amounting on single items of material to tens and even to hundreds of thousands of dollars or more a year.

Chemists sometimes forget that their science deals with energy no less than matter and that in fact chemistry as a science began with the recognition of the principles, materials and products of combustion. They have allowed the mechanical engineer to usurp many things which properly come much more directly within their own province. The combustion of coal is a typical chemical process. The selection of the most efficient coal and the determination of the conditions necessary for its most efficient combustion are essentially chemical problems. Chemical problems also are those arising in the manufacture of producer and illuminating gas, their utilization in gas engines, the development of power from the waste gases of the blast furnace, the adaptation of conditions to the proper handling and burning of peat, lignite and waste coal, the thermometric exploration of coal piles to forestall spontaneous combustion, smoke abatement, the control and improvement of fireroom conditions by draft regulation, flue gas analysis, temperature measurements and even the placing of firemen on the bonus basis. Taking power plant practice

and the conditions of coal purchase as they stand, the properly equipped chemist should be able to increase the efficiency of power production from five to thirty per cent.

The analysis of boiler compounds as an end in itself presents little to excite enthusiasm, but when such analyses are made the means of saving \$3600 a year in the power plants of a single company they take on a new and larger aspect, not only in the mind of the chemist but in the mind of the chemist's client.

The chemist who attacks the problems of power production will not hesitate to go outside the laboratory and take his property wherever he finds it. He will conduct boiler and engine tests, study the efficiency of grates and stokers, familiarize himself with the marvelous promise of the low-pressure turbine as an agent in efficient power production. While straining every resource of his science to produce steam economically by the combustion of coal, is it common sense for the chemist to stop there in ignorance of the fact that the efficiency of that steam can be increased at once from 25 to 100 per cent. by coupling a low-pressure turbine to the exhaust?

The distribution of power supplies problems no less directly within the province of the industrial chemist. He may begin with the analysis of lubricating oils. He proves his own inefficiency if he stops there. He must inform himself regarding the market prices of oils used elsewhere for similar service, the adaptability of the oils in question to application to the bearing by soaked waste, sight feeds, or gravity cups. He must be prepared to interpret his analysis in terms of practice and to follow the oil through the plant in order to prescribe conditions which shall keep down waste. There are few plants in which the industrial chemist working along these legitimate lines cannot save from 20 to 60 per cent. of the entire lubrication account, while the oil analyst has to his credit merely a few figures which his client probably fails to understand.

The efficiency and life of bearing metals varies over an extraordinarily wide range. Some are merely the refuse from type foundries, others are so carefully adapted in their composition to the requirements of particular service as to show an efficiency fifteen times or more as great as that of inferior materials. Here again the mere analysis means little, the practical question is "Which is the more efficient metal under the conditions imposed by practice?"

Much additional might be said regarding the opportunity before the chemist when any material concerned in power transmission is the subject of his study, whether it be leather, rubber or canvas belting, belt dressing, insulating material, trolley wire, trolley ears or trolley wheels. In every case it is within his power to create new standards of efficiency.

Similarly the industrial chemist has a large control over the efficiency of labor. He may increase this efficiency, that is, the output of the individual laborer, by supplying more efficient processes as Bessemer did in case of steel, Tennant in case of bleaching, or Le Blanc and Solvay in the manufacture of alkali. He may raise the efficiency of the laborer through education as when firemen are instructed in proper firing methods or when cooks in the sulphite pulp mill are given boiling schedules; in one instance within our knowledge such schedules raised the efficiency not of the cooks alone but of the entire plant as well, over 50 per cent.

Nowhere has the industrial chemist greater scope for the effective exercise of his trained and organized common sense than in the control of processes and the elimination of wastes and nowhere are the results he has already obtained more valuable. Their influence upon productive industry has been dramatic and profound. One need not say to chemists that the whole art of modern steel-making is under the strictest chemical control, or quote Carnegie to the effect that it has been revolutionized thereby. No industry affords a better example of the value of such control or furnishes more striking

instances of the profitable utilization of wastes. The conversion of slag to cement and fertilizer, the development of 10,000 horse power from the waste gases of a single furnace, are but steps in the development which will soon make pig iron the by-product of the furnace which derives its chief revenue from the waste of yesterday. With the open-hearth furnace still utilizing less than 10 per cent. of the energy of its fuel, let no chemist think the door of opportunity has closed.

Two factors of the first importance in their bearing upon industrial efficiency remain to be considered. They are:

The maintenance of standard in product.

Cheap transportation.

To mention them in this assembly is to bring before the minds of almost every one of us the endearing personality, the noble character and the splendid, comprehensive service of the friend we have just lost, Dr. Charles B. Dudley. Wherever his name is known, wherever material is bought on specifications which protect alike with scrupulous fairness the interest of seller and consumer, wherever standardized equipment safeguards life and property in railway travel, there is every reason but no need to speak in eulogy of what the chemist has accomplished in these regards.

From whichever viewpoint the relation of the chemist to the problems of production is studied it becomes clear that to take his proper place in the world of industry he must learn to know not only matter but material, and material under the strains and stresses of actual practice and with the limitations which commercial conditions impose. To the refinements of the laboratory he must add, as he is already adding in constantly increasing measure, the broader touch and larger method of the engineer; and finally, he must recognize that to reach his highest plane of service he must study men as well as things.

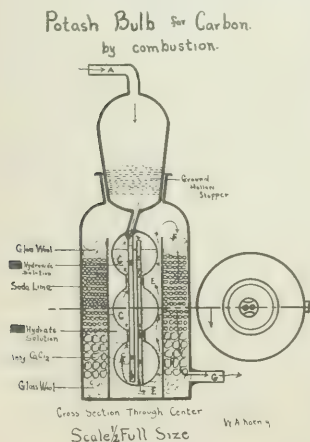
## NOTES AND CORRESPONDENCE.

### POTASH BULB FOR CARBON BY COMBUSTION.

The Mohr, Winklers-Liebig and all the potash bulbs thus far invented and in present use are of such complicated open structure that it is extremely difficult to properly clean them before weighing. With the Liebig this is less true than with the others, but it is necessary to weigh a separate piece of apparatus along

with it. We believe that this piece of apparatus overcomes these difficulties and is as efficient if not more so than any that have preceded it. Its weight filled with the chemicals is from 60 to 75 grams.

The course which the gas takes is shown by the arrows. Entering at A it passes through the hollow stopper and tube B B into the bulbs C C C which contain 1.3 caustic potash. It ascends to the top bulb and goes down through the tube D D, out into the cup E E, also



half-filled with 1.3 caustic potash. Rising to the top of E E it goes out into the bottle F F, passes down through soda lime and anhydrous calcium chloride and finally out at G.

One of these bulbs has been made by an expert glass-blower. It has been tested and gives results which do not vary over 0.0005 gram.

N. A. KOENIG.

### THE DETERMINATION OF MOISTURE BY DISTILLATION.

As is well known it is frequently impossible to determine with accuracy the moisture in substances by simply drying in a steam, water or hot air oven because of volatility of some ingredients or the oxidation of some constituents of the sample. Even when a current of carbon dioxide is used, it does not in all cases overcome the difficulties.

In the case of the determination of water in tars, a method of distillation has been in general use for some time. Light hydrocarbons such as toluene and xylene have been added to such tars to aid in carrying over the water. In the case of tars, because of their particularly viscid character and the danger of bumping and frothing special distilling arrangements have also been advised.<sup>1</sup>

Other suggestions for the determination of water by distillation have been made by G. Testori,<sup>2</sup> who determined the water in molasses by distilling 50 grams with 200 cc. of turpentine and caught the condensed water in a graduated cylinder. He claimed this procedure to be more accurate than ordinary oven-drying.

J. Marcussen<sup>3</sup> proposed determining water in oils, fats, soaps, resins, etc., by distillation with an immiscible liquid. Water-saturated xylene was used as the liquid to carry over the water in distillation. The water was caught in a 100 cc. graduate which would not insure very great accuracy in the operation.

The estimation of moisture in creosote oil by Arthur L. Dean<sup>4</sup> is based upon the work of Marcussen, but provides for more accurate measurements of the condensed waters.

Graef<sup>5</sup> also determined the moisture in lignite by distillation with naphtha.

The object of the writer in carrying out his experiments upon the determination of water in various substances by distillation was to see if a general method of procedure could be found for the determination of water in substances for which an oven test is not accurate or is too slow in giving a constant weight.

The writer for a number of years past has made moisture tests by distillation on samples of tar, crude camphor, hide grease and oils in which water was either suspended or emulsified and had tried at different times toluene, xylene (dry- and water-saturated), unfractionated coal tar solvent and benzene. It was thought best to extend some of the more recent experiments so as to make the work more general in character.

**Description of Method.**—The receiver selected was similar to that adopted by Dean and consisted of a tube of glass of about 5/16 inch inside diameter and graduated in cubic centimeters and tenths. Ten cc. are marked off and should be about 10 inches lineally on the tube or 1 cc. per inch. At a little above the 10 cc. mark, the tube is flared out funnel- or bulb-shaped (with open top) sufficiently large to hold 250 cc.; it is best not to have a stop-cock at the bottom, a device that was tried by the writer but found to be liable to leakage.

Sufficient substance is very carefully sampled and quickly covered with 200 to 300 cc. of benzene in an Erlenmeyer flask holding 16 ounces (500 cc.). The amount taken will generally be 25 or 50 grams depending upon the moisture content.

The water line on distillation should come in the upper half of the graduations if possible. The flask is then connected to a

<sup>1</sup> H. W. Jayne, *Jour. Amer. Chem. Soc.*, **25**, 814 (1903). E. Senger, *Jour. fur Gasbeleuchtung*, **45**, 841 *Jour. Soc. Chem. Ind.*, **1902**, 1475.

<sup>2</sup> *Staz. Sperim. Agric. Ital.*, **37**, 366-9; *Chem. Central.*, **1904-2**, 562-3.

<sup>3</sup> *Mitt. K. Materialprufungsamt.*, **23**, 58 (1905).

<sup>4</sup> U. S. Dept. Agr. Forest Service Cir., **134** (1908).

<sup>5</sup> Graef-Braumkohle, 1905.

Liebig condenser with a bent glass tube or goose neck, a thermometer registering up to 200° C. inserted and dipping into the benzene and the receiver placed in position. The receiver should be freshly cleaned each day it is used, with bichromate and sulphuric acid washing mixture, rinsed and thoroughly dried and filled up to the bulb with benzene such as is used in the distillation. The flask and goose neck should be covered with asbestos or cloth for insulation.

As it takes quite an appreciable time to drive the water from the interior of the particles or mass under analysis it is best not to distil at first but to hold the benzene in the flask, which is heated by means of an oil bath at a temperature of about 110–120° C. for about 1 to 2 hrs. The water then collects in the upper part of the flask, goose neck and condenser. The distillation should then be started and run at a regular rate of about 1 drop per second. At this rate the water will all come over before the benzene gets too hot and the latter as it distils does not seem to emulsify very appreciably with the water.

To test whether all the water has come over, the apparatus should not be disconnected until cold when drops would be seen in the upper part of the flask and goose neck if the water was not all off.

Some of the benzene should be poured back into the flask in such a case and the operation repeated.

At the end of the operation a plug of cotton on the end of a wire is wetted with benzene and pushed through the condenser from the upper end to send any drops of water into the receiver, that may have lodged in the condenser and then to rub any drops from the sides of the funnel into the measuring tube and finally to squeeze out the cotton as water may adhere to it in spite of its being saturated with an immiscible liquid.

The following table of analyses are given to show the results obtained with the use of this method with some comparative tests with water-saturated xylene and oven tests at 100° C.

Analyses.	Distillation tests.			Oven tests.	
	1. Per cent.	2. Per cent.	3.	1. Per cent.	2.
Egg albumen.....	15.90	15.35	.....	15.70	...
Cheese.....	29.75	29.90	.....	29.25	29.51
Butter.....	11.48	11.88	12.08 (xylene)	12.25	13.22
Linseed meal A.....	5.90	5.90	4.70	5.83	5.72
Linseed meal B.....	12.00	11.80	.....	9.85	...
Sawdust.....	17.2	...	13.2 (xylene)	16.5	...

From the experience the writer has had with moisture tests by distillation he is of the opinion that a benzene boiling approximately between 300°–450° F. makes the most suitable medium for driving over water and greater application should be found for such means of water determinations in organic substances where oven tests at 100° C. are not likely to be accurate because of oxidation or loss of volatile constituents.

SAMUEL S. SADTLER.

LABORATORY OF SAM'L P. SADTLER & SON,  
PHILADELPHIA.

#### A NEW REAGENT BOTTLE.

The annoyance of stoppers sticking, of having to wipe off dust from the lips of reagent bottles and of having the liquid spurt over the test tube instead of into it led to the construction of a new form of reagent bottle which I feel will be of interest to the practical chemist. The cut shown of this form requires but little description.

The conventional stopper is replaced by a cap ground on to an enlarged portion of the neck of the bottle. The cap is dome-shaped, made in two forms with and without a mushroomed top. The dome interior makes it possible to use a cork, if so desired, in case of exceedingly volatile liquids. This cap stopper

has the following advantages over the conventional glass stopper:

(a) It shields the lips from dust.

(b) It never comes in contact with the liquid hence does away with danger of contamination and sticking, the outside collar catching the drop or so of liquid that might adhere to the lip and run down on the outside.

(c) The stopper can be placed on the desk without soiling it.

The throat of the neck is peculiarly planned. The liquid in flowing through the channel has but little impetus hence will flow along the trumpet-shaped lip and thus be guided into a small test tube instead of spurting over it.

Furthermore the enlarged throat admits air even though the bottle be full, so that the liquid flows in a steady stream.

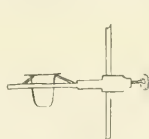
A German firm has undertaken to manufacture the bottle, and I trust it will soon be available for the general market.

MORNINGSIDE COLLEGE,  
SIOUX CITY, I.A.

WILFRED W. SCOTT.

#### CRUCIBLE AND SUPPORT.

For more than a year the writer has used a crucible and support made in a manner which will be clear by reference to the enclosed sketch.



Crucible with flaring rim  
Supported on three pegs  
of Plat.-Irid. wire.



The flaring rim of the crucible adds much strength; the support is more stable and the flame has an uninterrupted play where it is most needed.

CHARLES E. SWETT.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### AMERICAN CHEMICAL SOCIETY.

BOSTON MEETING, DECEMBER 27–31, 1909.

For a general account of the meeting the reader is referred to the Proceedings of the Society published in the February number of the *Journal of the American Chemical Society*. The meetings of those Divisions devoted more particularly to applied chemistry are reported in detail in these columns.

### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS, AMERICAN CHEMICAL SOCIETY.

BOSTON MEETING, DEC. 28–31, 1909.

The meeting was called to order, Mr. A. D. Little in the chair, Tuesday, Dec. 28th.

Mr. Little announced the appointment of the several committees which had been authorized at the Detroit meeting.



## COMMITTEE ON DEFINITION OF TRADE TERMS:

Clifford Richardson, *chairman*.  
J. B. F. Herreshoff.  
Geo. P. Adamson.

## COMMITTEE ON TRADE CUSTOMS

Henry Howard, *chairman*.  
Maximilian Toch.  
T. B. Wagner.

## COMMITTEE ON OFFICIAL SPECIFICATIONS:

Harvey J. Skinner, *chairman*.  
Rudolf de Roode.  
F. G. Stantial.

## COMMITTEE ON RESEARCH PROBLEMS:

Geo. C. Stone, *chairman*.  
W. R. Whitney.  
G. W. Thompson.

## COMMITTEE ON STANDARD METHODS OF TECHNICAL ANALYSIS:

T. J. Parker, *chairman*.  
James O. Handy.  
T. S. Gladding.

## COMMITTEE ON DESCRIPTIVE BIBLIOGRAPHIES:

Clement W. Andrews, *chairman*.  
Adolf Voge.  
A. M. Patterson.  
H. W. Craver.

## COMMITTEE ON PUBLICITY:

Wm. McMurtrie, *chairman*.  
W. D. Richardson.  
A. D. LITTLE.

SPECIAL COMMITTEE TO CONFER WITH MANUFACTURERS FOR THE PURPOSE OF DETERMINING AT WHAT PRICES ELEMENTS AND SPECIAL COMPOUNDS CAN BE OBTAINED PROVIDED A LARGE MARKET IS DEVELOPED FOR THEM:

Gellert Alleman, *chairman*.  
W. R. Whitney.  
M. C. Whitaker.

The following papers were then read:

1. W. D. Richardson. "Practical Corrosion Tests of Iron."
2. W. D. Richardson. "Methods for Testing Commercial Anhydrous Liquid Ammonia and Results."
3. James Otis Handy. "A Convenient Method of Refrigeration for Analytical and Industrial Investigations at Low Temperature ( $-75^{\circ}\text{C}.$ )."
4. Horace C. Porter and F. K. Ovitz. "Losses in the Storage of Coal."
5. Edward Hart. "The Present Condition of the Birch Oil Industry in the United States."
6. C. F. Mabery. "Lubrication, Lubricants—Oils, Greases and Solids."

In the third paper Mr. Handy exhibited a Thermos bottle with  $\text{CO}_2$  snow which he put in half a glass of acetone. This produced a low enough temperature to freeze mercury in a test tube placed in the mixture.

The reading of the papers was followed by interesting discussion. In the discussion following paper (4) the author said that methane was given off from the coal continuously seven or eight months. He considered that this had an important bearing on the spontaneous combustion and explosion of coal in storage. Following Mr. Mabery's paper it was stated that cylinder oils were not used by the Navy in the trip around the world. Straight hydrocarbons are preferred by the railroads. The railroads, however, use grease very largely in spite of the fact that it introduces a large friction loss.

The meeting then adjourned to take advantage of the several excursions scheduled for the afternoon.

WEDNESDAY, DECEMBER 29TH.

At the General Meeting of the Society Mr. Little, representing the Industrial Division read an address on "The Chemist's Place in Industry."<sup>1</sup>

THURSDAY, DECEMBER 30TH.

One of the most noteworthy attractions of the Division during the meeting was the Symposium on Paint, both on account of the papers presented and the discussion they brought forth. The following papers were presented at the morning session:

George C. Stone. "Manufacture of Oxide of Zinc."  
G. W. Thompson. "Scientific Preparation and Application of Paint."

Carl F. Woods. "Variations in Car Painting Practice."

In the paper on "Zinc Oxide," Mr. Stone described in an interesting manner the different processes now used, conditions effecting variation in the product, grading of the oxide and considered its use as a paint constituent. Mr. Thompson's paper was a vigorous plea for better definition and use of the term "scientifically prepared" as relating to commercial products, particularly paints. A lively discussion following the paper was participated in by Messrs. Gardner, Boova, Law, Whitney, Walker, Little, Fireman, Sabin, Stone, Richardson and the author. The following abstracts are from this discussion:

MR. GARDNER: Certain paints have no doubt a very firm basis and justification for the use of the term "scientifically prepared" for the following reasons: Two years ago the Paint Manufacturers' Association set up some special test fences at Atlantic City upon which were tested out various paint combinations. Those tests after being continued for a year were examined by the American Society for Testing Materials, under whose supervision they were erected, and the report of that Society gave to the manufacturers the opinion upon which they are basing their manufacture of paints to-day. These so-called "scientifically prepared" paints are paints made of more than one pigment, white lead and zinc oxide with a small proportion of either silica or barytes or asbestine or some other so-called inert pigment as reinforcements.

The general conclusion is that the admixture of more than one or more than two pigments makes a paint far superior to that manufactured from one alone. The manufacturers have manufactured paints containing four or more pigments, such as white lead and zinc oxide up to 90 per cent. and silica and barytes, which are so-called reinforcing pigments, and have obtained in that way a combination in which they claim to have a minimum of voids. These are the so-called scientifically prepared paints.

DR. THOMPSON: Because a pigment contains three different sized particles or three different original pigments it is not necessarily scientifically prepared, and the statement as made that these are all scientifically prepared paints is a remarkable statement without any basis of foundation.

MR. LITTLE: This whole discussion brings out to my mind very clearly indeed the value of the committee recently appointed, authorized by the Division, on the definition of trade terms and I think that we might with profit refer that term "scientific preparation" to that committee for a definition.

DR. FIREMAN: But a few years ago when I began to inquire into and consult with various paint authorities, they told me that the most important thing in the paint was the vehicle and not the pigment. Lately you don't hear much about the vehicle; it is all pigment. I have been thinking a little of the vehicle myself. I haven't noticed that the paint makers have made use of linseed oil of different thicknesses at all. It may be the situation could be very much improved by using linseed oils prepared of different consistencies.

DR. SABIN: I should like to say a few words, unofficially, in regard to what has been done by Committee E of the American

<sup>1</sup> See "Addresses," this issue.

Society for Testing Materials. This matter that Dr. Fireman has just brought up, the Committee is at work on and we hope in the fulness of time to have some specifications which will define linseed oil and also linseed oil boiled to different degrees.

In regard to those test fences, it is undoubtedly true, as has been said, that the work was in a way under the supervision of Committee E. Committee E was invited to inspect the Atlantic City fence. They saw the fence before the paint was put on and after it was erected. I am not aware that the Committee or Sub-Committee was invited to give a plan or anything of that sort, but they saw the fence after it was erected. It was all right. They also went there and saw part of the actual painting done. They have been there several times and looked at the fence and they have expressed a very guarded and reserved opinion as to what that fence appears to show, and it is not fair to the Committee to say that the opinion of the Committee is shown by the certain extracts because one part of the report was modified by other parts.

Committee E had painted the Pennsylvania Bridge at Havre de Grace a few years ago and that painting was done not under ideal conditions, but it was excellently done, so well done that while there are 19 different kinds of paint on that bridge, they are all in very good condition indeed after two or three years' exposure, so good that you cannot get people to agree at all as to any serious difference among them. Now everybody knows that there must be a great difference in paint there, but they got the paint applied so well that the poorest of those paints has stood all right. If you are going to have a test of paint, you have to eliminate accidental errors in painting. Paint men are all agreed that the paint must be applied under favorable conditions of temperature and of humidity. All paint manufacturers say in their circulars that paint should be applied at a temperature of over 50° F., and better at about 70°. The paint that was applied to those panels at Atlantic City was applied in midwinter, in a building in which the temperature went down probably below freezing a good share of the time. They didn't wait until the middle of summer to do it under more favorable conditions because they didn't want to wait forever to get some sort of a beginning. The paints were all applied as nearly as possible under similar circumstances, but they were not any of them applied under ideal conditions. Now when the paint was sent there it was sent by different manufacturers, and each manufacturer was asked to prepare that paint so that it should be as nearly right as possible according to his best judgment. I suppose the paint was made so that it was about right to apply at 60° or 70°. It was applied at a much lower temperature. The expert painter of the Paint Manufacturers' Association had to put turpentine into all those different paints to thin them down to what he considered a desirable consistency, and it was very far from being a fair test. It was very well for a beginning, but to say that they settled the whole business is totally absurd. Another thing which I think we are all agreed on is that the durability of a paint depends a good deal upon the kind of drier you put into it. The Committee was given in a general way the formulae of those paints, the kind of pigment, amount of oil and turpentine and amount of drier. Each one of those different paint manufacturers put in a drier that he was accustomed to use and most of them put in a drier which they bought from somebody else; they didn't know what it was made of and we certainly didn't know the remotest thing about it. I believe the only right way to put lead and manganese into oil is, not by the old and well-established method of melting up your oxide of manganese and lead with oil until it combines, or with rosin until it combines, because by that means you afterwards have an uncertain residue of lead and manganese which has not combined. Make a soap of the oil or, if it seems desirable, of the rosin. Then precipitate that with acetate of lead or chloride of manganese. Driers made

in that way furnish a lead and manganese soap which you can dissolve in oil or in turpentine, or even in benzine, and there are some advantages in using benzine. In that way you could know exactly how much manganese and lead there is in a good paint with that drier and it is made under uniform conditions.

DR. RICHARDSON: As far as scientifically prepared material, whether paint or any other substance, is concerned, it would seem to me that it is anything which is prepared on the basis of a theory which has been evolved by any laboratory study of any subject or by experience derived from service tests, whether the theory be correct or whether the service tests be erroneously interpreted. The intention of any one to prepare according to theory and service tests and not merely on rule of thumb would seem to me to entitle such preparation to be called scientifically prepared.

Adjourned 2 P.M.

The afternoon session was called to order by Mr. Little, who called upon Dr. Morris Loeb to explain somewhat the plans of the Chemists' Club. Dr. Loeb gave a brief résumé of the purpose and usefulness of the Club to the chemists of the country. In order to carry out this usefulness to its greatest extent, a building is being erected where the Chemists' Club will be housed. The building is really intended to serve as a central building for chemists of the whole country.

W. H. Walker presented his paper on "Paint Films as Accelerators to Corrosion of Iron." The next papers were by Charles A. Hertig and E. J. Newell on "The Determination of Oil in Flaxseed Products by the Specific Gravity Method," and by R. H. Gaines on "Bacterial Activity as a Corrosive Influence in the Soil."

Dr. Gill took the chair at the request of Mr. Little. The reading of papers continued.

Albert Sommer. "New Methods of Asphalt Examination."

H. E. Howe. "A New Precision Centrifuge."

The following papers were read by title:

A. C. Fieldner and J. D. Davis. "Some Variations in the Official Determination of Volatile Matter in Coal."

W. H. Boynton and H. C. Sherman. "The Temperature Reaction and Oil Mixtures with Sulphuric Acid."

H. C. Sherman and D. A. Bartlett. "A Comparison of the Accuracy of Different Formulae for Calculating Fuel Values."

Charles H. Ehrenfeld. "Action of Liquid Anhydrous Ammonia on Rubber Gaskets."

Charles S. Palmer. "A Simple Viscosimeter."

J. S. Staudt. "The Oxidation of Iron and Steel and How to Prevent It."

Henry Fay. "The Effect of Non-Metallic Impurities on the Properties of Steel."

FRIDAY, DECEMBER 31ST.

The Nominating Committee reported that the following nominations for officers had been made:

A. D. Little, *Chairman*.

Geo. C. Stone, *Vice-Chairman*.

F. E. Gallagher, *Secretary*.

*Executive Committee:*

W. H. Walker.

J. O. Handy.

A. S. Cushman.

C. P. Van Gundy.

W. D. Richardson, *ex officio*.

Upon motion duly seconded these nominees were accepted and thereafter unanimously elected by vote of the Division.

The remaining papers of the program were read as follows:

J. T. Baker. "Incompatibilities in Chemical Manufacture."

Francis G. Benedict and Harold L. Higgins. "An Adiabatic

Calorimeter for Use with the Calorimeter Bomb." (Read by Mr. Higgins.)

S. W. Parr. "The Weathering of Coal."

S. W. Parr. "A New Gas Calorimeter."

A. M. Comey. "The Correct Melting Point of Trinitrotoluene."

The paper by Charles P. Fox on "Guayule Grinding Experiments" was transferred to the Section of India Rubber Chemistry.

Mr. Baker's paper brought forth much discussion on the applicability of theory and laboratory results to large scale operations participated in by Mr. Little and Mr. Griffin and the author. Mr. Higgins exhibited the calorimeter described in his paper. This possessed many clever mechanical arrangements. In the discussion Mr. Parr pointed out that variations in the oxygen used for calorimeter work was a factor of some importance not generally appreciated. During the discussion of the paper on the weathering of coal the point was brought out that although there was a considerable loss in heat value there may occur an increase in the weight of the coal on an ash- and water-free basis.

A paper was read by Mr. G. E. Marion on the "Library as an Adjunct to the Industrial Laboratory." He described in detail the library system used in connection with the laboratory of Arthur D. Little, Inc.

The amount of time devoted to the papers and discussion and the necessity of an early adjournment left but little time for the experience meeting similar to the one so successfully held at Detroit. Members presented items of interest which would have gained circulation in no other way, while others found ready answers to questions that had arisen in connection with their work. Although space will not permit a reprint of all these experiences, the spirit of the meeting can perhaps be well shown by one extract from the record.

MR. BRADY: Mr. Chairman, I have been listening to what these gentlemen have said and I regret that they don't tell their names so we might know what industry they are connected with. I feel that I could bring out my point by this: when Dr. Whitney introduced me to Mrs. Whitney last evening, he said, "this is Bill Brady, of the Illinois Steel Co." I wish everyone here could get so well acquainted that he would know me as "old Bill Brady."

MR. LITTLE: Well, Bill, I suggest that we each tell in a word or two about himself and what his interests are.

B. T. BABBITT HYDE,  
*Secretary.*

#### DIVISION OF FERTILIZER CHEMISTS, AMERICAN CHEMICAL SOCIETY.

BOSTON MEETING, DECEMBER 30, 1909.

The meeting was called to order by the Chairman, F. B. Carpenter.

The Secretary reported an enrolment of 106 in the Division, including a representation of State Chemists and Directors as well as chemists associated with numerous fertilizer manufacturers. The spirit of cooperation between the State Chemists and the Fertilizer Manufacturers exists, and the work which can be carried on together in the Divisions should prove of great mutual advantage.

The report of the Committee on Nitrogen was then read, received and accepted.

REPORT OF THE COMMITTEE ON NITROGEN, PAUL RUDNICK,  
*Chairman.*

Three samples of nitrogenous material were prepared for this work. One was a sample of dried blood, another a tankage, and the third a mixture of the dried blood from the same lot which was used in the first-mentioned sample with acid phos-

phate and sulphate of potash. These samples were prepared with the greatest care to insure uniformity.

The letter of instructions accompanying the samples contained a request to determine moisture and nitrogen by the method or methods in regular use by the analyst addressed, and to describe the method used, as well as to answer a list of questions intended to bring out the conditions observed in some detail.

About sixty-five sets of samples were sent to those who indicated their willingness to cooperate, and reports were received from about forty-five. The great mass of figures included in these reports, and the fact that the great majority were of necessity received only within the last two or three weeks, has precluded the printing of a detailed and full report in time for this meeting. Before such a report is made, further study of the results must be made carefully, and in many cases it seems that further investigation of individual results will perhaps clear up doubtful points.

The results of the moisture determination are very unsatisfactory. Omitting a few obviously erroneous results, the difference between the extremes is still close to 1.4 per cent. in each of the three samples. This only serves to emphasize the importance of the determination of moisture, and the important rôle which this constituent plays in comparing analytical results. A difference of 1.4 per cent. in moisture makes a difference of practically 0.2 per cent. in the nitrogen content in the sample of dried blood.

Two factors seem to be chiefly responsible for a large part of this difference. One is the difference in the relative humidity of the air, the other the difference in ventilation facilities of the drying ovens. The importance of further work on this subject is self-evident.

The determination of nitrogen gave much more satisfactory results. After omitting a few results, as in the case of the moisture, where it was evident that the technique was faulty in some respects, the large majority showed an extreme variation of approximately 0.4 per cent. in the case of the blood and the tankage, and of approximately 0.2 per cent. in the case of the mixed fertilizer. These figures refer to the averages of the results of the individual analysts on samples as received, no allowance being made for differences in moisture content.

The Gunning method gave a slightly higher total average than the Kjeldahl method, and the so-called Kjeldahl-Gunning method gave a slightly higher average than the Gunning method.

It is important to note that low results were usually reported with a shorter time of digestion than the average. This would indicate the necessity of requiring a minimum time of digestion after the liquid has reached its final color.

The results by the absolute method are, as a whole, very unsatisfactory. These materials are apparently not suitable for the absolute method under the conditions ordinarily observed.

Under the circumstances this Committee recommends that a further study be made of the results obtained, that publication of the detailed results be deferred until all the reports which can be obtained, are received and that opportunity for further work upon these samples be afforded to those interested before a final report is made.

For the Committee on Phosphoric Acid, Mr. G. H. Farnham, Chairman, reported that the work had been on the determination of insoluble phosphoric acid.

The samples worked on by the collaborators were an acid phosphate, a 3-20 bone and a mixed fertilizer.

A table of results was displayed which showed many interesting features.

Different methods of filtering were used. Startling differences in results were shown in the case of the sample of bone.

The full report of the committee will be published later when all returns are in.



Mr. J. E. Breckenridge reported for the Committee on Potash. The following letter had been sent to each of the collaborators.

DEAR SIR:

A sample of fertilizer has been sent you by same mail. If possible, will you test it by the following methods?

Method No. 1: Official method for water-soluble potash as stated by the A. O. A. C., allowing solution having had the ammonia and ammonium oxalate to stand only long enough to cool before filtering, not over 4 hours, or stating in your report the time the solution stood before filtering.

Method No. 2: Weigh 2 grams on to a 11 cm. filter paper and wash with small portions of hot water into a 200 cc. flask, allowing each washing to run through before adding the next, until about 175 cc. are in flask. Add to washings in the flask about 2 cc. HCl (conc.). Heat to boiling, add ammonia and ammonium oxalate as usual, cool at once, make to mark and filter. Proceed as in official method, evaporating at least 50 cc.

Method No. 3: Weigh 20 grams into 500 cc. flask, boil gently with 450 cc. of water for 30 minutes, cool, make to mark and filter. Take 250 cc. of filtrate in 500 cc. flask, add 200 cc. of water, heat to boiling, add ammonia and ammonium oxalate as usual, cool, make to mark and filter. Take 50 cc. of filtrate, evaporate and proceed as in official method.

Also, if possible, test by methods No. 1, No. 2 and No. 3 some other samples of fertilizers which you may select from among samples which you have, selecting those which you think have low by official method.

Kindly make report in full and give any experiences in potash work which you care to relate. Send report to J. E. Breckenridge, Carteret, N. J., by December 1st, if possible.

The following results were reported on the official samples:

Analyst.	Method Nos.			
	1.	2.	3.	4.
Frank B. Kunst, West Va. ....	(a) 10.13	10.08	9.95	.....
Ag. Exp. Station. ....	(b) 10.14	10.08	9.95	.....
	(c) 9.97	10.04	10.14	9.96
J. Frank Morgan. ....	10.04	10.05	10.09	9.85
R. I. Exp. Station. ....	10.05	9.82	9.88	9.88
C. H. Jones. ....	9.82	10.04	10.14	.....
Vt. Ag. Exp. Station. ....	9.82	9.88	9.96	.....
O. M. Bishop, Va. Pol. Inst. ....	9.87	9.75	9.70	.....
H. C. Painter, Va. Pol. Inst. ....	9.80	9.80	.....	.....
J. A. Bizzell, State Col., Ithaca, N. Y. ....	9.84	9.93	9.78	.....
H. D. Haskins, Mass. Ag. Exp. Station. ....	9.94	9.93	9.99	.....
P. K. Nisbet, A. A. C. Co. ....	9.70	9.86	9.79	.....
F. B. Porter. ....	.....	9.97	10.06	.....
Atlanta, Swift & Co. ....	9.96	10.03	10.07	.....
	.....	99.9	10.13	.....
W. D. Richardson. ....	9.84	9.92	9.94	.....
Swift & Co. ....	9.85	9.95	9.95	.....
J. S. Rogers. ....	9.89	9.95	9.87	.....
B. of Chem., Wash., D. C. ....	9.88	10.04	.....	.....
R. Henry, V. C. C. Co. ....	9.85	9.97	9.83	.....
	.....	9.94	.....	.....
P. Rudnick. ....	10.03	10.02	10.13	.....
Stillwell & Gladding. ....	9.73	9.78	9.82	.....
Cascosyne & Co. ....	9.90	9.88	.....	.....
Wm. P. Dunne. ....	10.12	9.90	9.90	.....
Morris & Co. ....	10.08	9.87	9.74	.....
C. Farnham. ....	9.82	10.00	9.98	.....
Jarecki Chem. Co. ....	9.75	10.00	9.96	.....
J. E. Breckenridge. ....	9.84	9.94	9.82	.....
A. A. C. Co. ....	9.90	9.94	9.93	.....
Average. ....	9.90	9.94	9.92	.....
Highest. ....	10.13	10.08	10.14	.....
Lowest. ....	9.70	9.78	9.70	.....
Difference. ....	0.43	0.30	0.44	.....

17 analysts—10 higher by Method 2, 6 higher by Method 1—same by Methods 1 and 2.

Method 1 is regular Official Method.

Method 2 is washing 2 grams on filter with hot water.

Method 3 is 20 grams + 450 water in 500 cc. flask filtered and 50 cc. of filtrate taken in 200 cc. flask—then Official Method.

#### REMARKS ON THE ABOVE RESULTS:

Frank B. Kunst, W. Va. Ag. Exp. Station, Morgantown, W. Va.:

(a) Regular methods. (b) 5-gram weight, allowed to stand over night before filtering. (c) 10-gram weight, allowed to stand over night before filtering. I think the regular method will give as good or better results than either of the other methods suggested.

Dr. B. L. Hartwell, Kingston, R. I.:

Method No. 4: Solutions were made with cold water, in a similar way as for water-soluble phosphoric acid; that is, 2 grams of fertilizer were washed on 9 cm. filter paper with about 250 cc. of water, the solution being made to 250 cc. mark. 125 cc. of filtrates were taken, 50 cc. of water added, the solution brought to boiling, ammonia and ammonium oxalate added, solution cooled and made to the 200 cc. mark and filtered. Conclusion that this gives low remarks. Method No. 3 presents difficulty of boiling 450 cc. in 500 cc. flask without boiling over.

J. H. Bizzell, Ithaca, N. Y.:

Method No. 2: Instead of 2 grams 2½ grams were used and made up to 250 cc. Method No. 3: 10 grams instead of 20.

H. W. Wiley, Chief, Bureau of Chemistry, Washington, D. C.:

Mr. Veitch tried out Method No. 2 without HCl a few years ago and found when fertilizer was washed on filter with successive portions of hot distilled water, the results on some samples were as high as those obtained by the Carpenter Method, but on others were no higher than by the Official Method. Letter Dec. 1st: It makes a difference how the sample is washed. Best results by just covering sample with water and not filling filter.

Official sample was taken from stock and was no special mixture. It contained no large amount of iron and aluminum phosphate, but had Am. sulfate 40 lbs. and nitrate soda 127 lbs. to ton.

Conclusions:

That on Official sample—all methods tried give satisfactory results.

This I believe is explained by presence of sulfate of ammonia and nitrate of soda in sample. However, Method 2 shows more uniformity having only difference of 0.30 per cent. while Official Method has difference of 0.43 per cent.

Recommendations:

Further work on samples having no sulfate of ammonia and nitrate of soda and having their phosphoric acid from acid phosphate carrying 5 per cent. or more of iron and aluminum.

#### REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION OF THE DIVISION OF FERTILIZER CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY.

To the Executive Committee and Members of the Division of Fertilizer Chemists:

Your Committee begs to report that it has had considerable correspondence during the present year in reference to the subject of fertilizer legislation, the principal point discussed being whether it would be advisable for your Committee to consider the question of national fertilizer legislation or state legislation or whether attention should be given both. Another point discussed has been the advisability of framing the outline of a Fertilizer Act which it might be desirable to introduce into those states which now have no fertilizer Law, but which in the near future may become consumers of fertilizer and hence will apply to their Legislature for acts governing the purchase of fertilizer. The subject of forming a joint committee with the fertilizer committees of the Association of Official Agricultural Chemists and the National Fertilizer Association was also discussed, but it was considered that it would be advisable to first reach a decision on the points mentioned above and also

to collect complete data in reference to the subject of fertilizer legislation, before attempting to form such a joint committee.

It is the understanding of your Committee that the Committee on Legislation of the National Fertilizer Association, after trying for some time to draft a model fertilizer bill, have given up the attempt. They state that "owing to the differences in local conditions and varying interests in different parts of the country, it was thought best not to attempt to try to form an ideal law that would cover all conditions, as this would be almost an impossibility, but better to simply tabulate the present laws in such a form that they could be used for ready reference without necessitating the individual members searching through the mass of reading matter that would be necessary to give the information that he needs." The National Fertilizer Association has published such a pamphlet which you all will find very convenient in the consideration of this entire subject of fertilizer legislation.

Your Committee was advised that a proposed National Fertilizer Bill had been drafted by the Committee on Fertilizer Legislation of the A. O. A. C. which was to be presented for the endorsement of that Association at their meeting which was held in Denver. This bill was modeled after the National Food and Drugs' Act and was largely tentative in character to be used as a basis toward starting some action by Congress in regard to National Fertilizer Legislation. At the Denver Meeting the Chairman of your Committee was present. Dr. H. W. Wiley, the Chairman of the Committee on Fertilizer Legislation, after reading his report made mention of this proposed National Fertilizer Bill but did not urge its endorsement by the Association. He recommends that the report of this Committee be adopted and that the Committee be discharged. Such action was accordingly taken by the A. O. A. C. With the discharge of this Committee, your Committee feels that there is but little likelihood that the subject of National Fertilizer Legislation will be again brought up for some time to come and that therefore the efforts of your Committee if desired by the Division to continue it, can best be applied in tabulating all of the obtainable data on the subject of fertilizer legislation and perhaps the framing of the outline of a fertilizer act, which it might be desirable to introduce into those states which have no fertilizer law, at such a time as such states contemplate fertilizer legislation and also when states which now have a fertilizer law contemplate changes in that law.

In different states at most every session of the state legislatures there are frequently bills presented, most of which are pigeon-holed by Committees, but some of which are vicious in character. It would perhaps be advisable for this Division to have a representative in each state who could keep this Committee thoroughly posted on new legislation proposed in his state. Such information would be of great value to your Committee in keeping its files up to date.

Respectfully submitted,

A. LOWENSTEIN, *Chairman*.

The report of Committee on Ammonium Citrate Solution was next received and accepted.

This Committee reported an attempt to carry out the recommendations of the last meeting, namely, to cooperate with Committee from A. O. A. C. on Ammonium Citrate solution.

The A. O. A. C. was asked to cooperate but did not appoint the cooperating Committee as requested by this Division at their last meeting in Denver.

The appointing of a Committee for work on moisture alone was discussed and referred to the Executive Committee.

The taking over the work on analysis of Phosphate Rock as begun by National Fertilizer Association was discussed and referred to the Executive Committee.

The matter of Standard Samples was referred to Executive Committee.

The following papers were read:

1. F. B. Carpenter. Chairman's address. Influence of Chemistry on Agriculture."
2. H. J. Wheeler. "Concerning After-Effects of Certain Phosphates on Limed and Unlimed Lands."
3. R. H. Fash. "New Method for Filtering Insoluble Phosphoric Acid."
4. C. F. Hagelorn. "Facts Brought Out Regarding Uniform Analytical Methods for Phosphate Rock through the Recent Work of the National Fertilizer Association's Committee."
5. F. B. Carpenter. "Note on the Determination of Phosphoric Acid by the Official Volumetric Method."
6. C. H. Jones. "Laboratory Methods for Organic Nitrogen Availability. (10 m.)."
7. W. D. Richardson. "The Improvement of Analytical Processes. (10 m.)."
8. E. B. Voorhees. "The Cost of Available Nitrogen in Commercial Fertilizers."
9. J. G. Lipman. "Bacteriological Methods for Determining the Available Nitrogen in Fertilizers."
10. F. B. Porter. "Accuracy in Taking and Preparing Mixed Fertilizer Samples."
11. John P. Street. "The Determination of Inferior Ammoniates in Commercial Fertilizers."
12. The following papers on program were not presented:
13. J. M. McCandless. "Neutralization of the Ammonium Citrate Solution."
14. A. W. Blair. "Notes on the Recovery of Waste Platinum."
15. H. A. Huston. "Method and Materials Used in Soil Tests."

Great interest was shown in these papers and discussion lasted beyond the time for adjournment.

The By-Laws as proposed were accepted.

A Nominating Committee was appointed by the chairman to nominate officers for 1916. Comm. A. Lowenstein, P. K. Nisbet, C. H. Jones.

For *Chairman*, F. B. Carpenter; *Vice-Chairman*, B. L. Hartwell; *Secretary*, J. E. Breckenridge; *Executive Committee*, F. P. Veitch, H. A. Huston, W. J. Gascoyne and P. Rudnick.

The above were elected.

J. E. BRECKENRIDGE, *Secretary*.

## DIVISION OF AGRICULTURAL AND FOOD CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY.

### BOSTON MEETING.

#### FIRST MEETING, THURSDAY, DECEMBER 30TH.

The meeting was called to order by the Chairman, Dr. W. D. Bigelow, at 11 A.M. There being no objections the Chairman made the election of officers for the ensuing term, a special order for 3.30 P.M. Thursday, December 30th.

On motion of S. H. Ross, a Nominating Committee of three was appointed by the Chairman, this committee being instructed to present nominations for officers for the ensuing term. The Nominating Committee was composed of Alfred Springer, Herman H. Hanson, and B. H. Smith.

In the absence of the Secretary of the Division, Dr. W. D. B. Penniman, the Chairman appointed M. Dorset acting secretary.

At the conclusion of this preliminary business the Chairman's address, entitled "The Construction and Installation of a Technical Laboratory," was delivered by Dr. W. D. Bigelow. At the conclusion of this address the following papers were read:

- Ellen H. Richards. "Application of Electricity to Apparatus for Water Analysis."
- Herman C. Lythgoe. "The Composition of Milk."
- P. H. Smith and J. C. Reed. "The Use of the Refractometer in Detecting Added Water in Milk."

Adjourned until 2:30 P.M.

#### AFTERNOON SESSION.

Meeting called to order at 2:30 P.M.

The following papers were read:

- W. D. Richardson. "The Separation of Colloids from Solution by Freezing and Some Practical Results."
- C. S. Hudson. "The Determination of Cane Sugar by the Use of Invertase."

H. A. Edson. "The Influence of Microorganisms upon the Quality of Maple Syrup."

E. B. Holland. "The Stability of Butter Fat."

At the conclusion of the last-named paper the Nominating Committee of three reported the following nominations of officers for the ensuing term: *Chairman*, C. D. Woods; *Vice-Chairman*, G. E. Colby; *Secretary*, B. E. Curry; *Executive Committee*, E. W. Hilgard, H. W. Wiley, J. P. Street, C. G. Hopkins.

Upon vote of the meeting the Secretary was instructed to cast the ballot of the Division for the candidates presented by the Nominating Committee. These candidates were declared elected unanimously to serve for the ensuing year.

The following papers were then read:

A. Lowenstein and W. P. Dunne. "The Influence of the Method of Drying on the Non-Volatile Ether Extract of Spices."

Harry E. Sindall. "Sampling of Ground Spices."

F. P. Mulliken. "The Identification of Mixed Coloring Matters in Foods."

The meeting was adjourned at 4:30 P.M. until Friday morning, December 31st.

Friday, December 31st, meeting called to order by the Chairman at 10 A.M.

The following papers were read:

S. C. Prescott. "Relationship between Bacteriological and Chemical Findings in the Examination of Milk, Water, and Food Products."

H. J. Wheeler. "Observations Bearing upon the Practicability of Certain Chemical Methods of Testing Soils."

M. X. Sullivan and F. R. Reid. "The Oxidizing Power of Soils."

The following papers were then presented in brief by M. X. Sullivan:

J. J. Skinner. "Oxidation Effects of Manganese Salts in Soils."

Edmund C. Shorey and Elbert C. Lathrop. "Variation in Methoxyl in Soil Organic Matter."

Oswald Schreiner and Edmund C. Shorey. "Purin Bases in Soils."

Oswald Schreiner and Edmund C. Shorey. "Pentosans in Soils."

The following papers were then presented by the authors:

Burt L. Hartwell and Wilhelm B. Quantz. "The Available Phosphorus in Soils Measured by That Found in Flat Turnips."

C. L. Alsberg and O. F. Black. "The Detection of Deterioration of Corn and Corn-meal, with Special Reference to Pellagra."

The two following papers which do not appear on the regular program were read by Dr. Pennington:

M. E. Pennington and J. S. Hepburn. "A Rapid Method for the Determination of the Acid Value of Crude Fat and Its Application in the Detection of Aged Foods."

M. E. Pennington and A. D. Greenlee. "An Application of the Folin Method to the Determination of Nitrogen in Meat."

The remaining papers on the program were read by title. These were as follows:

A. L. Winton. "Microscopical Examination of Spices and Food Products."

Edward Gudeman. "Analysis of Maize Products (Starch, Syrups and Sugars)." (15 min.)

C. A. Browne. "Sampling of Sugar."

W. L. Dubois. "The Composition of Canned Peas and Lima Beans."

P. F. Trowbridge and C. R. Moulton. "Composition of Cold Water Extracts of Beef." (10 min.)

P. F. Trowbridge. "Phosphorus in Flesh."

H. C. Gore. "The Cold Storage of Apple Cider."

H. C. Gore. "The Value of Peaches as Vinegar Stock." (5 min.)

H. C. Gore and Alice L. Davison. "The Composition of Vinegars Formed from the Ciders of Different Varieties of Apples." (10 min.)

R. W. Balcom. "The Examination of Vinegar."

F. C. Cook. "The Estimation of Glycerine in Meat Preparations." (10 min.)

F. C. Cook. "A Comparison of Meat and Yeast Extracts of Known Origin." (10 min.)

C. A. Browne. "The Working Efficiency of a Constant Temperature Laboratory for Polarizing Sugars."

Edward Gudeman. "Analysis and Composition of Milk Products."

H. C. Sherman and A. Gross. "Delicacy of the Ferric-Chloride and Jorissen Reaction for Salicylic Acid." (5 min.)

P. F. Trowbridge. "Factors which Influence the Digestion of Food."

W. W. Skinner and G. W. Stiles. "Aeration a Factor in the Purification of Water."

J. A. LeClerc and Sherman Leavitt. "The Influence of Environment on the Composition of Wheat." (15 min.)

Fred W. Morse. "Rate of Acceleration of Plant Growth with Increase in Temperature." (10 min.)

A. E. Vinson. "The Stimulation of Premature Ripening by Chemical Means." (5 min.)

Arthur W. Dorr. "The Development of Catalase in Lower Fungi." (5 min.)

G. S. Fraps. "Wax of Candelilla or Mexican Wax Plant."

G. S. Fraps and N. C. Hammer. "Formation of Ammonia-soluble Organic Matter in Soils."

A. W. Blair. "Nitrates in Pineapple Soils."

H. E. Barnard and W. B. McCabe. "Some New Formulas for the Determination of Dextrose, Dextrine and Maltose."

H. E. Barnard and I. L. Miller. "A Study of the Keeping Qualities of Crushed Fruits, Fruit Syrups and Sugar Syrups."

H. E. Barnard. "The Composition of So-called Temperance Beers."

Wilfred W. Scott. "The Efficiency of Land Plasters in Preventing the Loss of Ammonia in Manures."

At 1 o'clock December 31st the meeting adjourned.

The Boston sessions of this Division were regarded as unusually interesting on account of the wide variety of subjects treated in the papers which were presented and also because of the very full discussions which were entered into by the majority of the members in attendance.

M. DORSET, *Acting Secretary of Division.*

## DIVISION OF PHARMACEUTICAL CHEMISTS, AMERICAN CHEMICAL SOCIETY.

### BOSTON MEETING.

The Pharmaceutical Division of the American Chemical Society at its recent meeting in Boston, Dec. 27th to 31st, held a very successful and profitable session. Numerous papers were presented and there was an interesting discussion in regard to the revision of the U. S. Pharmacopoeia. This was led by Dr. Geo. D. Rosengarten, Chairman of the delegates from the American Chemical Society to the Convention for the Revision of the Pharmacopoeia meeting in Washington in May next. It was decided by the Division upon motion of Prof. J. P. Remington, Chairman of the Committee of Revision of the Pharmacopoeia, to ask the delegates from the Society to the Revision Convention to present a written report to the Convention embodying the views of the American Chemical Society upon the whole subject of revision of the Pharmacopoeia.

Considerable time was occupied in completing the organization of the Division. Since the Summer meeting of the Society the Council has formally approved the formation of the Division and at the Boston meeting it was necessary therefore to adopt by-laws. They were adopted.

Officers as follows were elected for the ensuing year: *Chairman*, Prof. A. B. Stevens; *Vice-Chairman*, Dr. J. M. Francis; *Secretary*, B. L. Murray; *Executive Committee*, Dr. Edward Krimers, Prof. J. P. Remington, together with the Chairman and Secretary.

The Chairman announced the following as members of the Committee on Uniform Methods of Analysis appointed since the summer meeting: *Chairman*, F. O. Taylor, Detroit, Mich.; L. D. Havenhill, Lawrence, Mass.; B. L. Murray, New York City, N. Y.; L. A. Brown, Lexington, Ky.; A. P. Sy, Buffalo, N. Y.

This committee, as reported by its Chairman, in seeking to take up work not specially covered by similar committees of other organizations, is just at present looking into methods of analysis of alkaloidal and inorganic salts, especially those of the Pharmacopoeia for which Purity Rubrics are given but for which no proper methods of assay are given.

B. L. MURRAY, *Secretary.*

## THE UNITED STATES PHARMACOPOEIAL CONVENTION.

The next decennial U. S. Pharmacopoeial Convention will take place in Washington, May 10, 1910. The purpose of this



convention, which meets every ten years, is to elect the Committee of Revision of the U. S. Pharmacopoeia (which undertakes the active work of revision) and also to formulate general instructions for the guidance of this latter body.

The Convention is an incorporated body, whose membership is made up of delegates from the following national associations: the American Medical Association, the American Pharmaceutical Association and the American Chemical Society; in addition, the membership includes representatives from the Medical Departments of the Army and Navy, and Marine Hospital Service, also delegates from incorporated medical colleges and medical schools connected with incorporated colleges and universities; incorporated colleges of pharmacy and pharmaceutical schools connected with incorporated universities; incorporated medical and pharmaceutical associations. The officers of the Convention of 1900-'10 are: Prof. H. C. Wood, M.D., Philadelphia, *president*; Prof. H. M. Whelpley, M.D., St. Louis, *secretary*; G. W. Cook, M.D., Washington, *treasurer*.

The actual labor of revision rests upon a committee of 25, of which Prof. J. P. Remington, of Philadelphia, is chairman. The business matters attending the publication and financial management are controlled by a Board of Trustees, the chairman of which is Chas. E. Dohme, of Baltimore.

The general convention which will be held next May, preparatory to the ninth decennial revision of the Pharmacopoeia, will be the most important yet held, owing to the very prominent part this work has occupied as the Government standard authority on the purity of drugs and chemicals in the enactment of the Pure Food and Drugs Act.

V. COBLENTZ.

#### FIFTH GENERAL MEETING OF THE WESTERN ASSOCIATION OF TECHNICAL CHEMISTS AND METALLURGISTS.

The fifth annual session of the Association was a three-day tri-city meeting held on the 6th, 7th and 8th of January, 1910 at Boulder, Golden and Denver, Colorado.

The Boulder meeting included a visit to the sugar factory at Longmont, Colorado, and general inspection of the laboratories and shops of the state university at Boulder. The sugar factory at Longmont is one of the largest and most modern in the state, and offered the visitors an opportunity to observe the latest and best practice in beet sugar manufacture.

At Boulder the chemical fraternity, Alpha Chi Sigma, provided an informal luncheon at the chemical laboratory at 6:30 P.M., after which the meeting convened for the reading and discussion of papers.

The following papers were presented:

Harry J. Wolf. "Chlorine Cells."  
H. B. Hallowell. "The Metallurgy of the Ores of Cobalt, Ontario, Canada."

A. L. Tatum. "The Use of the Immersion Refractometer in Standardizing Solutions."

R. R. Knowles. "The Mineral Waters of Steamboat Springs, Colorado."

The second day's meeting at Golden included a visit to Coor's brewery and inspection of the shops and laboratories of the state school of mines. The Integral Club extended the use of its club rooms, and the faculty of the school tendered a supper at 6:00 P.M.

Following this, a meeting was held in Stratton Hall of Metallurgy for the reading and discussion of papers. The following papers were presented:

J. E. Edwards. "Notes on Ore-Roasting."

A. O. Kellogg. "The Partridge Hot-blast Furnace."

Dr. Herman Fleck. "The Search for Radium-bearing Minerals."

J. C. Bailar. "Review of Industrial and Manufacturing Chemistry."

V. H. Gottschalk. "Review of Analytical Chemistry for 1909."

The third day of the meeting was devoted to visits to smelters and chemical manufacturing industries of Denver, these trips having been arranged to suit the preference of those in attendance. In the evening was held the fifth annual banquet at the Auditorium hotel. At this meeting Dr. W. D. Engle delivered the president's annual address on the "Progress in Theoretical Chemistry during 1909."

The entire meeting was interesting and successful from every point of view and showed the progress which the Association is making in handling the problems of Western chemistry and metallurgy.

#### RECENT PATENTS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, solicitor of patents, McGill Building, Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts* to which publication the reader is referred.

943,132. **Electrolyte and Method of Electrodepositing Nickel.**  
EDWARD F. KERN. Patented Dec. 7, 1909.

This electrolyte and process of electrodepositing nickel therefrom are founded upon the discovery that a smooth, dense, coherent and adherent deposit of nickel can be obtained by the electrolysis of a solution of fluo-silicate of nickel, preferably associated in the bath with ammonium fluorid or ammonium fluorid and aluminum fluo-silicate.

The following is stated to be preferred composition of the electrolyte:

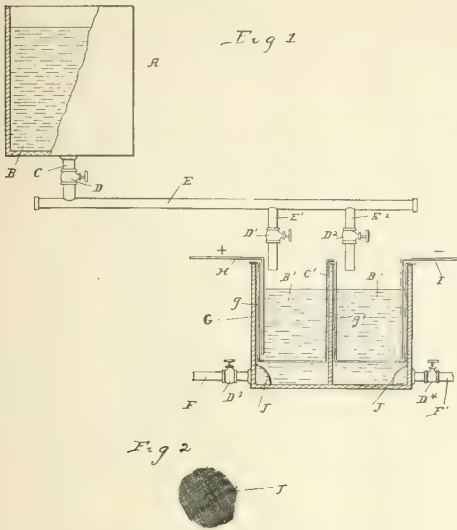
Water.....	100 parts.
Fluo-silicate of nickel.....	10 parts.
Ammonium fluorid.....	5 parts.
Aluminum fluo-silicate.....	5 parts.

942,207. **Process of Treating the Spent Liquor of Paper Mills.**  
I. KRISSE. Patented Dec. 7, 1909.

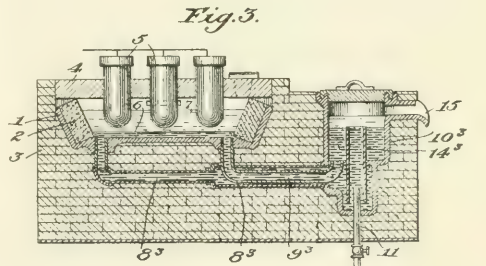
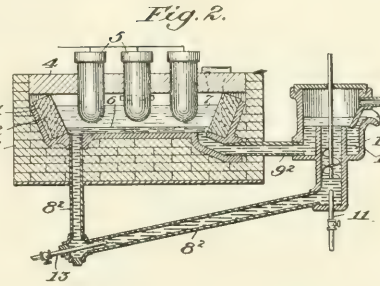
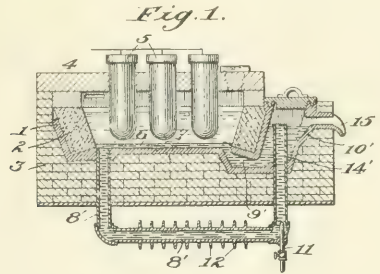
This invention relates to a process of treating the spent liquor of paper or pulp mills, so as to be enabled to extract from such spent liquor the caustic or alkali, and also to extract from said liquor the resinous and allied substances, and it is the further object of the invention, to prepare the reclaimed caustic or alkali in a manner so as to impart to the same the causticity necessary for its reemployment.

One of the methods of practicing this process is as follows: spent liquor is made the electrolyte in an electrolytic apparatus, consisting of two compartments, a positive compartment and a negative compartment, preferably separated from each other by a porous septum. Each of these compartments is provided with an electrode; the electrode of the negative compartment may consist of copper, iron or lead or other suitable conductor, but the electrode of the positive compartment should consist if possible of a material not injuriously affected by the electrolyzing action of the current. The negative electrode or the electrode contained in the negative compartment is connected to the negative pole of the charging circuit, and the electrode contained in the positive compartment is connected to the positive pole of the charging circuit. In a short time, the test will show that the contents of the negative compartment has acquired a stronger alkaline reaction than the contents of the positive compartment.

After the current has passed through the electrolytic apparatus for a sufficient length of time, it was found that all the alkali had accumulated in the negative compartment and all the acid



injected gas. The nitrid resulting from the reaction, being



in the positive compartment, but the liquid in the negative compartment remained surcharged with various matters and it needed a second process to clarify this liquid.

The illustration shows a preferred form of apparatus for use in the practice of the process.

**943,132. Process of Producing Nitrids.** CHARLES E. ACKER. Patented Dec. 14, 1909.

This process relates to the electrolytic production of nitrids, especially those of the alkali and alkaline-earth metals.

The process comprises the steps of electrolyzing a molten compound of the metal which is to be combined with nitrogen, alloying the separated metal with a cathode metal, reacting on the alloyed metal with a nitrogenous gas, and returning the residual metal to the cathode. Incidental steps are the injection of the nitrogenous gas in a direction to cause or assist the circulation of the alloy and residual metal; and the cooling of the alloy before treatment with the gas, especially by maintaining opposed adjacent streams of the alloy and residual metal.

The apparatus illustrated has the general construction of that heretofore devised by the inventor for the production of caustic alkali, the electrolytic cell comprising a cast-iron vessel 1 lined at the sides with magnesia brick 2, enclosed in brickwork 3 and covered by a refractory slab 4, through which pass the depending carbon anodes 5. In the bottom of the vessel is a shallow layer 6 of a molten heavy inert metal such as lead, constituting the cathode, upon which is the molten electrolyte 7. The vessel 1 is connected by delivery and return pipes or ducts 8, 9 to a separate chamber 10, into which the nitrogenous gas may be introduced by a valved pipe 11. The delivery pipe 8 is provided with a series of annular heat-radiating flanges 12, to cool the alloy therein. The circulation of the alloy and metal may be effected either solely by the current of injected gas, or by a mechanical device, or by both. If desired, the alloy may be cooled by injecting a regulated amount of a cooled and compressed gaseous reagent.

The reaction chamber 10 is of the general construction of that employed in the inventor's caustic alkali apparatus, comprising a vertical central pipe 14, which receives the molten alloy and

usually lighter than the residual metal, rises and collects as a floating layer, which may be run out through a suitable outlet 15, the metal returning to the electrolytic cell to reconstitute the cathode.

**944,481. Process and Apparatus for Artificially Aging or Seasoning Portland Cement.** THOMAS A. EDISON. Patented Dec. 28, 1909.

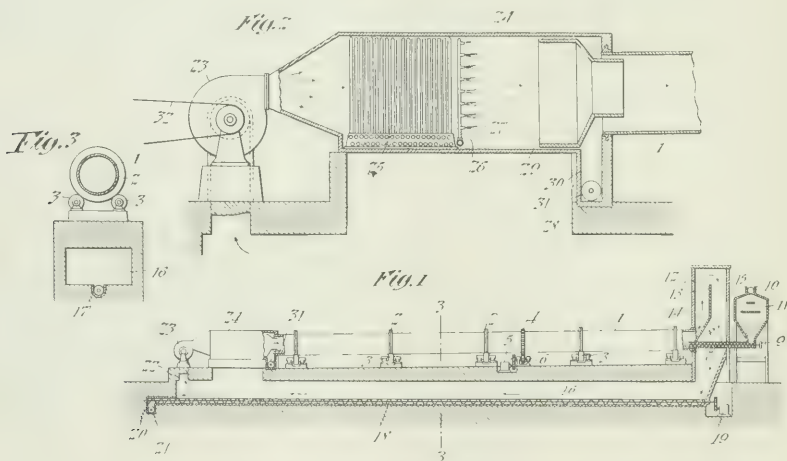
Under the present practice, in the manufacture of Portland cement, the freshly ground material is stored in a suitable stock house and is permitted to age or season until it is in condition to be used in construction work or to be submitted to the ordinary tests. The absorption of atmospheric moisture is a slow operation, depending entirely upon the temperature and hygroscopic condition of the air, so that the operation requires considerable time.

The object of this invention is to provide a process and apparatus by which this treatment may be performed artificially so that the seasoning or aging of the cement may be effected

within a short time and at the same time conduct the operations under such exact control that the quality of the product may be regulated within very close limits and the raw material may be treated absolutely independently of the weather conditions, which factor does not need to be considered in the carrying out of the invention.

The material to be treated, consisting usually of freshly ground or crushed cement clinker, is fed into the upper end of the cylinder 1, by a screw conveyor 7, which occupies a horizontal tube 8, the inner end of which extends into the end of the cylinder 1 in close proximity to the bottom thereof. The conveyor 7 may be continuously driven by a belt applied to the pulley 9 and material is continuously supplied thereto by a conveyor 10, which discharges into the feed receptacle 11, the bottom of which communicates with the outer end of the conveyor 7. The upper end of the cylinder 1 communicates with a chamber 12 having a partition 13 which divides the same into the ascending and descending flues 14 and 15, the lower end of the flue 15 opening into a horizontal flue or settling chamber 16, of greater cross-section than the interior of the cylinder 1. The bottom of the settling chamber is formed with a longitudinal trough 17, within which is a spiral conveyor 18, driven by the motor 19. Below the discharge end of the conveyor 18 is a transverse trough 20 and conveyor 21 for removing the deposited material from the settling chamber.

introduced into the upper end thereof, by the conveyor 7. The blower 23 is continuously driven by a belt 32, and supplies a blast of air to the chamber 24. The air blast passes around and between the pipes 25, which are heated by steam passing therethrough, and steam is admitted to the hot blast from the jets 27. The gases consisting of hot air, substantially saturated with water vapor, pass through the contracted end of the pipe 29 into and through the cylinder 1, along with the ground cement is passing in a continuous body, by reason of the rotation and inclination thereof. The cement is showered through the hot gases, being carried up from the bottom of the kiln, on account of its rotation, until it falls from the side of the kiln to the bottom, whereby the fine particles are thoroughly exposed to the action of the heated gases passing through the cylinder. The bulk of material passes through the cylinder from its upper to its lower end, discharging in a continuous stream into the chamber 30 from which it is removed by the conveyor 31. A considerable percentage of the ground material is, however, carried by the blast through the flues 14 and 15, into the settling chamber 16, where, on account of its increased cross-section, the velocity of the blast is checked and the material settles to the bottom of said chamber, and is removed therefrom continuously by the conveyors 18 and 21. The heated air from which the moisture has been extracted by the ground cement then passes through the passage 22 and enters the blower 23,



The exit end of the settling chamber 16 communicates through a passage 22 with the interior of a rotary exhaust fan or blower 23 which delivers a blast into the chamber 24. Within this chamber and extending across the path of the blast is a set of steam pipes or coils 25, and beyond said steam pipes is a pipe 26, for admitting steam into said chamber in the form of a series of jets 27. The chamber 24 is stationary and rests upon the foundation 28. In its forward end is a shouldered pipe 29, for reducing the cross-section of the blast, the contracted end of said pipe extending into the lower end of the rotary cylinder 1, which end fits within a circular opening formed in the end of the chamber 24. Below the pipes 29, and communicating with the end of the cylinder 1, is a discharge chamber 30, for receiving material delivered by the cylinder, and at the bottom of said chamber 30, is a screw conveyor 31 for continuously removing the material therefrom. The cylinder 1 is continuously rotated and ground Portland cement is continuously in-

by which it is driven through the apparatus again in the same manner as before. The air passing through the blower is still at a high temperature and therefore there is an economy effected in the amount of heat which must be supplied by the steam pipes 25 since the same particles of air are used over and over again, only such fresh air being used as is necessary to balance the air lost through leakage, the fresh air being drawn in automatically by the blower 23. The temperature of the air may be regulated by the steam pipes 25 and should be between 150 and 250° F., preferably about 200° F., as it leaves the chamber 24. The material removed from the apparatus by the conveyors 31 and 21 may be discharged into a storage warehouse where it is held a sufficient time to permit a reduction of the amount or degree of exterior hydration of the particles by a slow hydration of the interior thereof by a sort of cementation or progression inward.



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## EDITORIALS.

### RUBBER CHEMISTRY.

At the Boston meeting of the American Chemical Society a Rubber Section was organized, the purpose of which is to bring together at occasional meetings chemists and others who are particularly interested in the field of India rubber. It had been felt that many problems of moment and interest to manufacturers and consumers could be solved by united effort. Notable among these problems and the first one to be undertaken is the standardizing of the methods of chemical analysis and physical test of rubber articles. To this end, a committee of ten was appointed by the chairman of the Section, Mr. Charles C. Goodrich. Dr. Charles Knight, of Buchtel College, Akron, Ohio, was elected chairman of the committee.

This committee has unquestionably undertaken a large contract. At present the methods are as numerous and diverse as the laboratories in which they are applied. To bring some degree of order out of such a chaos is a task worthy of the best effort. It is clearly the express duty of this committee to do definite work as well as to indulge in discussion, and above all to recommend procedure that can be used tentatively, at least, until modified by experience. The use of uniform methods and good ones will be of distinct service to the rubber industry.

This is not the first attempt to work out reliable methods of rubber analysis, nor is it the only committee now at work. Cordial coöperation from manufacturers and consumers will do much to surmount the numerous difficulties, and if every one who has occasion to analyze or test any of the articles made of India rubber will freely place their experience and data at the service of the committee, will try proposed methods and will adopt for use recommended methods, even if not perfect, the success of the movement is assured.

W. C. GEER.

## ORIGINAL PAPERS.

[CONTRIBUTION FROM PITTSBURGH LABORATORY, TECHNOLOGIC BRANCH, UNITED STATES GEOLOGICAL SURVEY.]

### LOSSES IN THE STORAGE OF COAL.<sup>1</sup>

By HORACE C. PORTER AND F. K. OVITZ.

Received January 10, 1910.

It is known from the work of Parr on Illinois coals, and that of Richters, Fayol, Boudouard, and others abroad, that coal undergoes a certain amount of oxidation and consequent deterioration in the air at ordinary temperatures. The Technologic Branch, U. S. Geological Survey, is engaged on a study of the extent of this deterioration of coal in the air under different climatic conditions, both as to loss in heating value and loss in value for the manufacture of gas, coke, and by-products. Whether such loss is with most coals and under average conditions serious enough to justify the expense of underwater storage seems to be an unsettled question.

However, since the Government spends over three millions of dollars annually in the purchase of coal in large lots for the Army and Navy and for the Panama canal, much of which must be stored for some time in tropical climates and under unfavorable conditions, the possibility of effecting the economy of even a small percentage of the heating value by improved methods of storing seemed to justify this investigation.

Parr found that Illinois coals exposed in 20-lb. lots to the weather for 7 months lost from two to ten per cent. of their heating value.<sup>2</sup> The Western Electric Company stored 9,000 tons of Illinois coal under water for 2 years and found that the same coal, after having been exposed to the weather during that time, had two per cent. less heating value than the water-stored coal.<sup>3</sup> The Municipal Gas

<sup>1</sup> Published by permission of the Director, U. S. Geological Survey.

<sup>2</sup> Parr, S. W., and Hamilton, N. D., *Econ. Geol.*, II, 693 (1907).

<sup>3</sup> *Eng. News*, 60, 729.

Works, at Stettin, Germany, reports a saving of eight per cent. on gas yield and thirty per cent. on ammonia by storing their coal under water rather than in the open.<sup>1</sup>

Coal contains humic bodies unsaturated with respect to oxygen and it therefore absorbs considerable quantities of oxygen, particularly during the period immediately after mining. Oxygen is in theory doubly depreciative in its effect on the heating value of coal since it is not only a diluent like ash but, by combining during storage of the coal, with the combustible constituents, carbon and hydrogen, it serves also to render them in part inert and unavailable as fuel. The heat of this slow combustion process is either dissipated by ventilation or accumulates when ventilation is restricted, thus giving rise to spontaneous combustion.

In the present investigation an effort has been made to ascertain the extent of this absorption of oxygen, together with the degree of deterioration caused thereby, and at the same time the extent of the liberation by coal of combustible gases during storage. A 5-gallon glass bottle, crated, was taken into the mine and 25 lbs. of coal (about  $1\frac{1}{2}$  in. in size) put into it immediately after stripping from the seam. The bottle was hermetically sealed and shipped to the laboratory. A sample of the air in the bottle was then drawn out by means of a tube provided for the purpose in the rubber stopper.

Out of 10 samples taken in this way of as many different types of coal only one showed any oxygen in the air of the bottle on reaching the laboratory. A sample of Connellsville coal which, on account of the proximity of the field, reached the laboratory only 36 hours after mining, showed after that time 11 per cent. oxygen in the air of the bottle. The other samples required from three to fifteen days to reach the laboratory and had absorbed during that time all the oxygen in the air of the bottle. It was then arranged, in case of four of these samples, to admit a measured supply of air or oxygen to the bottle (at the top) and to withdraw (from the bottom) the altered air containing gases from the coal. Sufficient air was introduced each day to give a slight excess of oxygen so that some oxygen was present in the gases withdrawn. In 5 months, ten kilos of the following coals absorbed oxygen as follows:

Sheridan Co., Wyo. sub-bituminous	24	1 liter oxygen from air
Saline Co., Ill.	19.2	"
Franklin Co., Ill.	57.0	"
Pocahontas, W. Va.	18.2	"

The absorption of oxygen has continued at a somewhat reduced rate since the expiration of the 5 months period, above described. The Franklin Co., Illinois, coal absorbed in 5 months oxygen equivalent to 0.81 per cent. of its weight. It seems probable, furthermore, that the conditions of open-air storage allow

more thorough circulation of air and cause a greater degree of oxidation than is the case in the laboratory method.

The gases drawn off contained a slight amount of  $\text{CO}_2$ , in one case (the Wyoming sub-bituminous) about one-tenth of what would correspond to the oxygen taken up and in the other cases much less than that amount. That this taking up of oxygen by coal is not merely a surface adsorption phenomenon as when charcoal absorbs gases was shown by Richters, who subjected the oxygenated coal to reduced pressure and boiled it in water when he obtained some  $\text{CO}_2$  but practically no oxygen. This experiment has been repeated in this investigation on the samples of Franklin Co., Ill., coal and the results obtained by Richters corroborated.

Rather remarkable quantities of methane were present in the gases drawn off from these sealed bottles of coal. The extent of this production of methane at ordinary temperatures by coal freshly mined seems to be in accordance with the tendency of the mine from which the coal was taken to give trouble with gas explosions. This fact therefore shows that the coal itself, as it lies in the seam, is liberating gas from its own substance in greater or less degree according to its character. The following percentages of methane found in the 5-gallon bottles of coal illustrate this point:

Coal from	Time in days since mining.	Per cent. $\text{CH}_4$ in air of bottle.
Hanna, Wyo.	37	15.0
Kentucky Cannel.	24	0.0
Monongah, W. Va.	31	47.2
Pocahontas, W. Va.	29	3.8
Saline Co., Ill.	25	47.0
Sheridan Co., Wyo.	28	5.7
Connellsville, Pa.	12	8.9
Franklin Co., Ill.	15	72.4

Disastrous mine explosions have occurred within the last few years at Hanna, Wyoming, Monongah, West Virginia, and at Ziegler, Franklin County, Illinois. The above results tend to show the gaseous character of the coal from these mines.

The Franklin County, Illinois, coal, apparently the most gaseous of those examined, has produced (from 10 kilos) in 5 months about 10 liters of methane. The loss of calorific value by such a loss of  $\text{CH}_4$  is very small, approximately 9,000 calories per kilo of coal, or from 0.1 to 0.2 per cent. Hydrogen could not be detected in the gases drawn off and  $\text{CO}$ , if present at all, was in traces only.

The loss of heating value through the absorption of oxygen by coal in storage may perhaps be more serious than that incurred through the loss of gases. A question is often raised in this connection as to the effect of change of weight during storage. For example, if a 1,000-ton pile of lignite carrying 20 per cent. moisture dries during storage to 10 per cent. moisture, we have only 900 tons remaining and the

<sup>1</sup> Seidl. *Ch. Gazd.*, 97, 322, 1909.

heat value per lb. may be greater than in the original coal. This complication, due to moisture changes, is, however, avoided if we calculate calorific values in every case to the ash- and moisture-free basis. We then confine ourselves to a determination of the alteration in the organic, fuel substance present. If we may assume that the total amount of this organic material does not change, there is no need of measuring change of weight of the coal. If, on the other hand, this organic material increases in weight due to simple addition of oxygen, our figures for loss of heat value neglecting changes in weight will be too high; and if the organic material loses in weight due to oxidation of hydrogen to water or of carbon to  $\text{CO}_2$ , our figures for calorific loss will be too low. Richters,<sup>1</sup> Boudouard,<sup>2</sup> Dennstedt,<sup>3</sup> and others have shown that coal increases slightly in weight when subjected to oxygen treatment and that unsaturated compounds in the coal add oxygen to their molecules and become saturated. The effect of oxygen therefore becomes merely one of neutralization of an equivalent in carbon and hydrogen in the coal and its diluting effect becomes of no consequence.

In the present investigation changes in weight have not been determined, either in the laboratory tests or the outdoor tests, and therefore the figures obtained for loss of heat value may be somewhat too high. The following table gives the results of determinations of calorific value on the coal in sealed bottles through which air or oxygen had been passed for several months; and also on samples of the same coal submerged under water and of the fresh coal as mined.

The following results show no deterioration of heat value during storage under water for 8 months except in case of the Wyoming sub-bituminous No. 44. After 22 months' storage under water, during the latter half of which time the bottles stood in a warm place, sometimes reaching  $100^\circ \text{F.}$ , the Pocahontas coal had lost 0.2 per cent. and the Saline Co., Illinois, coal, 0.7 per cent. By the passage of air or oxygen through the coal, the Pocahontas has lost 0.6 per cent., the Wyoming 0.7 per cent., and the Saline Co., Illinois, 1.1 per cent. In case of the Franklin Co., Illinois, coals the results are not reliable, since the mine samples were not taken at the same time as those in bottles, and one of these mine samples (the W. Frankfort) shows lower heat value than the sample from the same mine kept 6 months in a sealed bottle. The test 23a, showing a loss by outdoor storage of 1.6 per cent. on the car sample value, the latter in turn being 1.1 per cent. lower than the mine sample value, indicates the greater tendency of coal to deteriorate by outdoor exposure than by treatment with a current of air in a bottle.

The Pocahontas coal in all cases evidently deteriorates less than the Illinois coals.

RESULTS OF LABORATORY STORAGE TESTS. TREATMENT OF COAL WITH AIR OR OXYGEN AND IMMERSION UNDER WATER.

Lab. No.	Description of sample	Calories calculated to ash- and moisture-free material.	Calories calculated to material free of M., S. and true ash. <sup>1</sup>	Per cent. loss.
<i>Pocahontas coal</i>				
38	Mine sample, sealed until analyzed	8804	8828	....
16a	Exposed 8 mo. outdoors in 20-lb. lot.....	8800	8839	....
16b	8 mo. under water in laboratory...	8802	8835	....
16c	22 mo. under water in laboratory...	8782	8814	0.17
37	10 mo. treated with oxygen in laboratory.....	8754	8776	0.57
<i>Sheridan, Wyo. sub-bituminous coal</i>				
45	Mine sample, sealed until analyzed.	7326	7381	....
44	7 mo. under water in laboratory...	7281	7335	0.62
43	7 mo. treated with air in laboratory	7274	7331	0.67
<i>Harrisburg, Saline Co., Ill., coal</i>				
40	Mine sample sealed until analyzed..	8272	8397	....
23	Car sample, exposed in transit 3 weeks.....	8200	8301	....
23a	Exposed 8 mo. outdoors in 20-lb. lot.....	8060	8170	1.59
23b	8 mo. under water in laboratory...	8210	8312	....
23c	22 mo. under water in laboratory...	8151	8239	0.75
39	Corresponds to No. 40, after 9 mo. air treatment ..	8204	8308	1.06
<i>Franklin Co., Ill., coal</i>				
125	Mine sample, Benton, taken 5 mo. after No. 49 ..	8071	8139	....
49	Bottle sample, Benton, treated 5 mo. with oxygen.....	8060	8141	....
123	Mine sample, W. Frankfort, taken 5 mo. after No. 48.....	8030	8108	....
48	Bottle sample, W. Frankfort, tightly sealed for 6 mo.....	8063	8130	....

In coöperation with the Navy, the Geological Survey has recently begun some tests on outdoor storage of coal. Fifty-pound portions were prepared from the same lot of coal which had been crushed to  $\frac{1}{2}$  in. size and thoroughly mixed. Some of these were submerged under salt water at Portsmouth, N. H., at Norfolk, Va., and at Key West, Fla., others under fresh water at Pittsburg, and still others exposed to the weather at each of the places mentioned. These portions will be analyzed periodically to determine loss.

The Survey is also sampling coal on the Isthmus of Panama as it is being piled in open-air storage and will take further samples after exposure for different periods in order to determine the deterioration in that hot climate.

About two years ago outdoor tests were started by the Geological Survey at Sheridan, Wyoming, to determine means of preventing "slacking" of "black lignite" or sub-bituminous coal and to determine the extent of deterioration in calorific value

<sup>1</sup> By true ash is meant the original ash with its water of hydration in clay and with its iron pyrites instead of the  $\text{Fe}_2\text{O}_3$  formed by burning. See Parr and Wheeler, THIS JOURNAL, 1, 636.

$$\text{Cal. value, unit coal} = \frac{W - 2620 \text{ S}}{1.00 - [M + A + 5/8 \text{ S} + 0.08(A - 10/8 \text{ S})]}$$

[W = calories as determined, M = moisture and A = ash as determined; the expression 0.08 (A-10/8 S) is used for Illinois and Western coals, and 0.06 (A-10/8 S) for Eastern coals.]

<sup>2</sup> From a mine in vicinity of that from which No. 40 was taken.

<sup>1</sup> R. Threlfall, J. Soc. Chem. Ind., 28, 759 (1909).

<sup>2</sup> O. Boudouard, Compt. rend., 148, 284.

<sup>3</sup> Dennstedt and Buenz, Z. angew. Chem., 21, 1825.



during slacking. It was found that slacking could be prevented in large degree by storing in tight covered bins, but that in both open and closed bins, with slacking and without, the coal lost in eight months about 5 per cent. of its heat value.

The laboratory investigation has shown that coal absorbs oxygen most rapidly immediately after mining. The sample from Saline Co., Illinois, for example, absorbed 2 liters or more of oxygen in the first four days after mining, and after five months the rate of absorption had decreased to approximately 0.7 liter in four days. This rapid absorption of oxygen just after mining suggests the advisability in order to avoid spontaneous combustion, of keeping fresh coal more or less open and cooled by ventilation until a proper time has elapsed after mining. Experiments are now being begun in the laboratory to show the comparative rise in temperature and absorption of oxygen by different coals on passing air through a sample a given length of time at 100° C. The effect also of fineness of division and amount of surface exposed on the absorption of oxygen is likely to be large and will be investigated.

To summarize the results of the investigation thus far accomplished, coal absorbs oxygen from the air during storage without forming  $\text{CO}_2$  and the amount of oxygen absorbed accords approximately with the deterioration in heat value. Oxidation may be largely prevented by immersion under water. Methane is evolved from freshly mined coal in quantities of importance as bearing on mine explosions but of no importance as a loss of fuel value. Outdoor tests are being conducted to determine the extent of the loss during storage in the open as compared with immersion under water. Laboratory by-product tests are being carried on to determine changes in the yields of gas, tar and ammonia through deterioration in storage.

## THE ANALYSIS OF BABBITT METALS; SOLDER AND JOURNAL BRASSES.

By D. J. DEMOREST.

Received January 22, 1910.

The separations involved in the analysis of these alloys of lead, copper, antimony, and tin as ordinarily carried out are long and tiresome. Furthermore, the results obtained are not always satisfactory.

In the analysis of alloys containing tin with lead and copper, but no antimony, the usual procedure is to separate the tin from the other metals as metastannic acid by means of nitric acid. This metastannic acid, however, is always contaminated with oxides of lead and copper and phosphorus, which cannot be washed out. The old method of removing these oxides is to fuse the  $\text{SnO}_2$  with sodium carbonate and sulphur and to dissolve out the sulphostannate formed, leaving the lead and copper as sul-

phides. Sometimes two fusions are required. This method is time-consuming and troublesome.

Experiments by the writer show that accurate results can be obtained in a short time by the following procedure: The metastannic acid is dissolved in  $\text{NH}_4\text{HS}$ , leaving the lead and copper as insoluble sulphides. This  $\text{NH}_4\text{HS}$  solution is electrolyzed, giving very accurately and quickly the amount of tin in the sample. The sulphides of lead and copper are added to the main solution of lead and copper, which is then electrolyzed.

This  $\text{NH}_4\text{HS}$  treatment of the metastannic acid with subsequent electrolysis is new, so far as the author is aware.

When antimony is present, as well as tin (as in type metals and babbitts), the nitric acid separation, as above mentioned, cannot be used because antimony is not rendered entirely insoluble by the acid. The old method of separation by means of alkaline sulphides has to be used. But this process, as given in various texts, consumes much time and, according to the author's experience, is very liable to leave some antimony and tin with the lead and copper. The results of many experiments, however, show that this method can be modified so as to give complete separation in  $3/4$  of an hour after the sample is weighed up, instead of two to four hours, as required by the ordinary way. The modification involves the solution of the sulphides of lead and tin in nitric acid and then precipitation of the lead and copper a second time as sulphides.

After the antimony and tin have been separated from the lead and copper, the standard method has been that of Clark<sup>1</sup> for the separation of antimony from tin. In this method the antimony is separated from the tin by precipitation by  $\text{H}_2\text{S}$  in oxalic acid solution and the sulphides weighed up. Also the method of Rose, modified by Hampe,<sup>2</sup> in which the antimony is precipitated as sodium antimoniate. But these methods are also long.

The results of experiments show that from an  $\text{NH}_4\text{HS}$  solution antimony and tin can be quickly and quantitatively precipitated together in a pure state electrolytically.

Further, it was found that the deposit can be dissolved from the electrode without loss, the antimony oxidized to  $\text{H}_2\text{SbO}_4$  and titrated accurately iodimetrically. The tin is obtained by difference. This precipitation of antimony and tin together, electrolytically, with subsequent titration of the antimony, is new so far as the author is aware.

The writer tried to use the method of electrolyzing the antimony and tin solution in a  $\text{Na}_2\text{S}$  solution, from which the antimony only is supposed to separate, but the process did not prove successful.

<sup>1</sup> Chem. News, 21, 124.

<sup>2</sup> Chem. Ztg., 18, 1900.

The whole process for the determination of lead, copper, antimony and tin can be completed easily in  $3\frac{1}{2}$  to 4 hours.

During the first part of this investigation, the writer used rotating anodes or cathodes in the electrolysis with good results. But there is some trouble in keeping good electrical connections with the rotating electrode unless an expensive mercury cup contact is used and in almost all the work on alloys containing both antimony and tin, stationary electrodes were used, one of which is a platinum gauze cylinder, 2" high and 1" in diameter, upon which the metals were precipitated. To hasten the precipitation the solution was agitated by means of a platinum paddle operated by a water motor. The deposits are all very adherent and dense. The motor was belted to a group of six stirrers, so that many different depositions can be carried on at once. Using a gauze cathode and rotating the solution in this way it is possible to deposit 0.300 gram of copper quantitatively in 10 to 15 minutes. A particular advantage of rotating the solution instead of the anode or cathode is that it permits the use of any style of electrode.

The methods in detail are as follows:

#### I. ANTIMONY NOT PRESENT (AS IN SOLDER AND JOURNAL BRASSES).

Two grams of the journal brass are dissolved in nitric acid (sp. gr. 1.42) and evaporated to dryness to bring the metastannic acid to such a condition that it will not clog up a filter paper. The use of a gentle air blast over the solution facilitates the evaporation. To the residue 50 cc. of water and 5 cc. of  $\text{HNO}_3$  are added, heated to dissolve the lead and copper, etc., and filtered. The metastannic acid on the filter is washed two or three times and then washed back into the beaker or flask in which the metal was dissolved. 25 cc. of  $\text{NH}_4\text{HS}$  (made by saturating  $\text{NH}_4\text{OH}$ , (sp. gr. 0.9) with  $\text{H}_2\text{S}$ ) are poured through the filter and into the flask. This will dissolve all the metastannic acid and precipitate as sulphides the lead and copper which contaminated the tin. The flask and its contents are heated and shaken for about ten minutes and then the solution poured through the same filter as before, catching the  $\text{NH}_4\text{HS}$  solution of the tin in a 300 cc. beaker. The sulphides on the filter are washed with water containing some  $\text{NH}_4\text{HS}$ . The filtrate is diluted to 200 cc. The small amount of  $\text{PbS}$  and  $\text{Cu}_2\text{S}$  is dissolved in a little nitric acid and added to the main solution of lead and copper.

One hundred cc. of the tin solution are pipetted off, 10 cc. of  $\text{NH}_4\text{HS}$  and 4 grams  $\text{KCN}$  are added and the solution electrolyzed with a 5- to 6-ampere current, rotating the solution as described below under the analysis of alloys containing both antimony and tin.

The solution of lead and copper is diluted to 200

cc., 50 to 100 cc. (according to the amount of lead present) are pipetted off, 15 cc.  $\text{HNO}_3$  added, and the solution is electrolyzed, using a 5- to 6-ampere current and rotating electrode as described below.

Any iron and zinc in the metal are left in the solution from which the lead and copper are deposited. If it is desired to determine these, the solution is evaporated to dryness, dissolved in a little  $\text{HCl}$ , the iron oxidized with  $\text{H}_2\text{O}_2$  and precipitated with ammonia. The filtrate from the iron is made strongly acid with  $\text{HCl}$  and boiled to decompose the  $\text{H}_2\text{O}_2$ . The solution is then titrated with  $\text{K}_4\text{Fe}(\text{CN})_6$ , using uranium acetate indicator.

The following are some results obtained by this method upon two samples of journal brasses:

	Wt. of Cu	Wt. of Pb.	Wt. of Tin.
No. 1.....	0.7592	0.1304	0.0701
	0.7590	0.1305	0.0705
	0.7592	0.1300	0.0703
No. 2.....	0.7856	0.1012	0.0909
	0.7866	0.1006	0.0905
	0.7842	0.1010	0.0905
	0.7844	0.1002	

#### 2. ANTIMONY PRESENT, (AS IN BEARING METALS).

One gram of the alloy is placed in a 200 cc. beaker and covered with 20 cc. of water. In this are dissolved 5 grams of tartaric acid and then 10 cc.  $\text{HNO}_3$  (sp. gr. 1.42) are added. This will dissolve the alloy quickly unless it is in large pieces, which it never need be. When dissolved the solution is diluted to 50 cc. and a strong solution of  $\text{NaOH}$  is poured in until the hydroxides first formed dissolve and leave the solution clear. The liquid should not be heated as this may cause a precipitate of metastannic acid to commence to form in the alkaline solution. The solution is poured slowly and with constant shaking into a flask containing 150 cc. of a boiling hot solution of 10 grams of  $\text{NaOH}$  and 10 cc. of a colorless saturated solution of  $\text{Na}_2\text{S}$ . (The solution should be colorless or some copper will remain in the solution.) The contents of the flask are agitated for several minutes and then allowed to settle. The sulphides of lead and copper will settle quickly and compactly. The clear solution is decanted as closely as possible through a strong filter paper folded in ribs. The precipitate is washed twice by decantation, using about 25 cc. of water each time.

Now to the sulphides in the flask 5 cc. of  $\text{HNO}_3$  are added and heated until the black sulphides disappear. Then the solution is made alkaline with  $\text{NaOH}$  again and 10 cc.  $\text{Na}_2\text{S}$  solution added and heated and shaken vigorously for several minutes. Again the supernatant liquid is decanted through the same filter, washed twice by decantation and then the sulphides transferred to the filter and washed twice more with hot water containing a little  $\text{Na}_2\text{S}$ .

The filter paper with its contents is placed in a crucible and heated gently so as to dry the sulphides.

While these are drying, sulphuric acid is added un-

der a hood to the filtrate which contains the Sb and Sn until the solution, which should have a volume of 400 to 500 cc., is acid. The liquid is stirred well and allowed to settle for a few minutes, then decanted through a filter paper as closely as possible to get rid of the greater part of the liquid. The beaker containing the sulphides of antimony and tin is set under the funnel, and 25 cc. of the  $\text{NH}_4\text{HS}$  solution diluted to 50 cc. are poured through. This will dissolve the sulphides. The solution is transferred to a 300 cc. beaker, diluted to 150 cc., 4 to 5 grams KCN are added, and the solution electrolyzed, the solution being rapidly rotated.

The cathode used was a cylinder of platinum gauze, 2" high and 1" in diameter. The voltage used was 8 to 10 volts and the current 5 to 6 amperes. This large current will heat the solution considerably and it is best to set the beaker in a basin of water. The KCN keeps sulphur from separating out on the anode in excess by forming KCNS with the polysulphides.

The tin and antimony should be deposited in 30 to 60 minutes, depending on the amounts present. The cathode is lifted out and washed first with water, then with alcohol, and dried on a steam plate. If any pieces of sulphur are entangled in the meshes of the gauze, dip the cathode in  $\text{CS}_2$  before washing with alcohol. This, however, is rarely necessary.

After weighing, the solution is again electrolyzed for ten minutes and the cathode washed and weighed. If the weight has not increased more than 1 mm. in these ten minutes the electrolysis is complete.

After the cathode is weighed it is placed in a small beaker and 5 cc. of strong  $\text{HNO}_3$  are poured over it from a pipette. The acid is heated and the beaker tipped and the electrode turned so that the  $\text{HNO}_3$  will dissolve off all the deposit that is possible. There will always be some black stains left on the cathode, which are very difficult to remove with  $\text{HNO}_3$ . The gauze is washed with a fine jet of water over the beaker. Then the gauze is set into another small beaker and 60 cc. of a strong HCl are poured over it, which will dissolve off the black stains. The  $\text{HNO}_3$  is used first to avoid the loss of antimony as  $\text{SbH}_3$ , which would take place if the deposit were dissolved in HCl alone.

The gauze is then washed with a jet of water into the HCl and the two solutions poured into a 500 cc. Erlenmeyer flask and the beakers washed with a little more HCl. The solution should be boiled vigorously for 10 to 15 minutes to decompose the  $\text{HNO}_3$ .

Or, instead of mixing the two solutions, the 5 cc. of  $\text{HNO}_3$  are evaporated to dryness in a platinum dish (for speed), then the residue is dissolved in 60 cc. HCl. This last way is the best but takes more time.

Now, to the hot HCl solution 5 grams of  $\text{KClO}_3$  are added in small amounts at a time, then 50 cc.

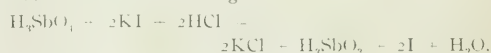
$\text{H}_2\text{O}$  are poured in and the solution boiled while passing through a stream of  $\text{CO}_2$  until the free chlorine is all gone, as shown by starch-iodide paper. This takes 15 to 20 minutes.

The  $\text{KClO}_3$  must not be added before the  $\text{HNO}_3$  is decomposed, for the  $\text{KNO}_3$  formed greatly prolongs the time necessary to get rid of all free Cl.

When the free chlorine is all gone water is added to make a volume of 150 cc. and the solution cooled under tap water while passing in a stream of  $\text{CO}_2$  to displace the air. The solution should be colorless. The  $\text{CO}_2$  is made from marble and HCl.

When cool, the current of  $\text{CO}_2$  is stopped, 4 grams KI are added and the liquid stirred until the KI is all dissolved. Then standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution is run in until the color due to iodine all disappears, starch solution is added, and the excess thio titrated back with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  until a blue color is obtained. This should take only a few drops. The writer prefers this end point to merely titrating with  $\text{Na}_2\text{S}_2\text{O}_3$  until the blue starch iodide disappears.

The  $\text{KClO}_3$  oxidizes the antimony to  $\text{H}_3\text{SbO}_4$ . This liberates iodine according to the reaction:



Then the thiosulphate is oxidized by the iodine in the reaction:



The writer standardizes the thiosulphate against  $\text{K}_2\text{Cr}_2\text{O}_7$  of known iron strength. Also by treating  $\text{Sb}_2\text{O}_3$  or Sb or tartar emetic by dissolving them in HCl and  $\text{KClO}_3$  and treating as above. The two methods of standardization check very closely. The iron strength of the bichromate, multiplied by 1.0751, gives its antimony value. The "thio" solution is made by dissolving 20.7 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and diluting to one liter. The author does not like the use of  $\text{SnCl}_2$  for the titration as it changes strength so rapidly.

There is nothing which can be deposited with the antimony and tin which will interfere with the process. Arsenic does not interfere.

While the electrolysis of the antimony and tin is going on, the dried sulphides of lead and copper are crumbled into a beaker, the paper burned and the ash added to the rest in the beaker. The sulphides and ash are dissolved in 40 cc. concentrated  $\text{HNO}_3$ . In this solution the lead may be determined as sulphate and the copper in the filtrate from the lead titrated by the iodide method. But it is much quicker and more accurate to determine the two electrolytically, according to the following:

The solution is diluted to 100 cc., 50 cc. are pipetted into a platinum dish, 50 cc. of water added and electrolyzed with a potential of six volts for a few minutes. The voltage is then increased to 10 to 12 volts,



keeping the solution stirred. The lead is all deposited on the dish, which is the anode, in about 15 minutes. Then part of the  $\text{HNO}_3$  is neutralized with ammonia and the electrolysis continued for 15 minutes, when the copper is all deposited on the gauze cathode. The electrodes are washed quickly with water, then with alcohol, dried and weighed. The  $\text{PbO}_2$  should be dried at above  $200^\circ \text{C.}$  to expel water.

To show that antimony and tin are deposited quantitatively the following results are given:

Present.				Found.			
Lead.	Copper.	Antimony.	Tin.	Sb + Sn.	Antimony	Tin	Cu
0.700	0	0.1500	0.1000	0.2513	0.1480	0.1035	..
0.700	0	.....	0.1000	0.2493	0.1495	0.1000	..
0.700	0.0500	0.1500	0.1000	0.2503	0.1490	0.1013	..
0.700	0.0500	0.1500	0.1000	0.2500	.....	.....	..
0.700	0.0500	0.1500	0.1000	0.2480	0.1480	0.1000	0.050
.....	.....	0.1800	.....	.....	0.1800	.....	.....
.....	.....	0.1500	0.1500	0.3005	0.1505	0.1500	.....
.....	.....	0.1500	0.1000	0.2493	0.1490	0.1005	.....
.....	.....	0.1500	0.1000	0.2513	0.1495	0.1020	.....

Present.				Found.			
Lead.	Copper.	Antimony.	Tin.	Lead.	Copper.	Sb + Sn.	Sb. Sn.
0.6500	0.050	0.1500	0.1500	0.6505	0.05050	0.2999	0.1496 0.1503

In this last analysis the thiosulphate was standardized against  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, giving as the strength of the thio 1 cc. = 0.00504 gram antimony. Then 0.200 gram of pure  $\text{Sb}_2\text{O}_3$  was dissolved in  $\text{HCl}$  and  $\text{KClO}_3$  and treated as in the regular process. Result, 1 cc. = 0.00504 gram Sb. This was then repeated except that 5 cc. of  $\text{HNO}_3$  were used as in the process. Result, 1 cc. = 0.00504 gram Sb.

The electric current used in the work at the Department of Metallurgy was obtained from an alternating current 110-volt lighting circuit rectified by means of a chemical transformer, designed by the writer, making use of the well-known aluminium method. The rectifier was able to transform 10 amperes for 60 hours without trouble and has been in use for a year without any repairs. The aluminium and lead electrode were each  $3\frac{1}{2}''$  by  $10''$  by  $3/8''$  and were immersed in a saturated solution of  $(\text{NH}_4)_3\text{PO}_4$  in glass cylinders around which water circulated. Four cells were used and connected as described in Perkin's "Practical Methods of Electro-Chemistry." 85 per cent. of the a. c. was rectified.

Almost all the experimental work on alloys containing both antimony and tin upon which the foregoing processes were based was done at the laboratory of the Department of Metallurgy of the Ohio State University. The rest was chiefly done at the laboratory of the Union Pacific Railroad at Omaha.

#### SUMMARY.

Antimony and tin may be separated from lead and copper by the alkali sulphide method in three-quarters of an hour.

Metastannic acid may be purified by dissolving it in  $\text{NH}_4\text{HS}$  and filtering off the sulphides of copper

and lead. This  $\text{NH}_4\text{HS}$  can then be electrolyzed for tin.

Antimony and tin may be accurately and quickly deposited together electrolytically from a solution of their sulphides dissolved in  $\text{NH}_4\text{HS}$ .

The deposit of antimony and tin may be dissolved off the electrode and the antimony oxidized to  $\text{H}_3\text{SbO}_4$  and titrated accurately.

Rapid electrolysis with excellently adhering deposits may be accomplished when gauze electrodes and mechanical stirring of the solution are used.

Alloys of lead, copper, antimony and tin may be accurately analyzed in three to four hours.

DEPARTMENT OF METALLURGY,  
OHIO STATE UNIVERSITY,  
Jan. 12, 1910

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC., LABORATORY OF ENGINEERING CHEMISTRY.]

## THE LIBRARY AS AN ADJUNCT TO INDUSTRIAL LABORATORIES.

By GUY E. MARION  
Received January 10, 1910.

It has been recently said:<sup>1</sup> "The financial library of the present day is a comparatively recent institution, and many causes have contributed to its development." Equally true is this statement in its application to the library as an adjunct to industrial laboratories. Let us review for a moment, then, the causes which have contributed to the usefulness and development of the Laboratory Library. Many of them are the same as those which are causing to spring into existence the increasing number of small specialized libraries about the country in general. The chief cause, however, is the phenomenal growth of all business, which continually necessitates the introduction of new methods for expediting its procedure. Specialization has entered here as elsewhere, and it has been found better to have one man prepared to answer the many inquiries of a general nature coming to the laboratory than to be forced to distribute these inquiries throughout the staff. This has meant, then, the collecting of the laboratory's resources (books, pamphlets, experimental data, catalogues, documentary experience, etc.) at one point into a library. In this way a new channel has been formed for the transaction of a portion of the laboratory's business, namely, the answering of the general inquiries arising both in and outside its ranks; and the library has become a vital factor in the operation of the organization. But, not only has the work been better systematized by the advent of the library; its coming has enabled the laboratory to accept wider opportunities, to enter with less hesitation new and unexploited fields, and to increase its efficiency in a large number of ways which make for confidence

<sup>1</sup> From a paper entitled "Some Aspects of a Financial Library," by Beatrice E. Carr, presented at the first annual meeting of the Special Libraries Association.

and progress; in fact, with its constant accumulation of the laboratory's daily experience, upon which no value can appreciatively be set, with its acquiring and classification of the ever-increasing amount of literature from without, it becomes, as the accumulated experience of the past, the base upon which the future rests. Another contributory cause to the existence of the library is the speed of present-day business. No longer can the chemist wait until he has an opportunity to consult the public library or other outside source of information. This method is too slow. He is supposed to know. That is why he is consulted by the business layman, and his knowledge must be forthcoming on the spot. So the library has come to his aid and enabled him to hold his layman often on the telephone wire while the desired information is found. Thus the chemist has embraced the library as an adjunct largely in self-protection.

Since these contributing causes are readily apparent, and the laboratory library as an institution already exists, it is for us to consider the specific nature of the demand made upon it (answering at the same time, if we can, why the public library does not fill the need), its limitations, the literature required and acquired, and then for a moment to look at a concrete example of such a library as we have in mind with its various working systems.

*Specific Nature of the Demand.*—The industrial laboratory needs a highly specialized library, at the same time one containing certain well-chosen general works. For example, its shelves must be rich with analytical works in almost every field, with books on explosives, beverages, foods, oils, gases, fuels, ceramics, textiles, paints, soaps, gums, essences, distillation products, metals, rubber, leather, wood, celluloid, etc. In fact, a small library of technology with only the best works chosen in each branch of industry fills best the need. For general works, it needs bibliographical books, transactions of the various scientific and learned societies, trade catalogues from the industries which the laboratory in question particularly serves, the current technical periodicals covering the fields claiming its attention, and a collection of general books on English, advertising, engineering, building, physics, chemistry, biology, botany, and manufacture, to which should be added reference lists, dictionaries, encyclopaedias, directories, maps, atlases, etc. Indeed the demand in the industrial laboratory library is both for a small commercial library as well as a highly specialized library of technology. It is because of this peculiar mixed nature of the demand that our public libraries cannot hope to meet it. They rarely give any attention to the commercial side of their development, and their general lay clientele forbids their building up along the technical and industrial lines beyond a few of the more general books. But what is still worse,

their distance most often militates against them. Moreover, the chemist in industry must have his works without fail when he wants them. It will not suffice to await their return from some other borrower from a library. The peculiar type of library to serve the interests of the laboratory must be able to hold its entire resources within certain prescribed limits so that it can recall them at a moment's notice.

*Its Limitations.*—What are its limitations? The people making use of it will rarely, if ever, exceed fifty in number. But these people, instead of being a desultory public are intensely active specialists, and bring to the library inquiries which require the best skill in their answering. In this way the library does not suffer from lack of quantity, for its interest is more than kept up by the increased quality sought in its work. Its purchases are also limited, and its accessions cannot be compared in numbers with those of the public library, for very few things are acquired which are not for a well-defined purpose. In spite of the narrower field and its restricting limitations, the laboratory library is still, however, a unique and purposeful proposition, changing the more general characteristics of a library to meet its changed surroundings.

*Literature Required and Acquired.*—We come now to the literature required and acquired, which prove in reality to be of two quite different classes. We have already explained above, in touching upon the specific nature of the laboratory library, what kinds of literature are required. They are chiefly textbooks, specialists' pamphlets, trade catalogues, reference works, maps, etc. These must be all purchased and are quite necessary. In distinction from these, there is a vast bulk of data which we may properly call acquired rather than required. It is made up of the information culled from the laboratory's daily correspondence, out of the experiences of the various members of the laboratory staff, from experiments carried on in the laboratory, from various technical reports and investigations made for clients; in short, it is made up of the accumulated results of the internal life of the laboratory itself. In fact, this acquired data is unquestionably for the laboratory library, the most valuable part of its information.

*Information Dept. of Arthur D. Little, Inc.*—Perhaps a more minute description of a concrete example of such a library as we have briefly described above in general terms will be more useful and suggestive to you. The Information Department of Arthur D. Little, Inc., which is entrusted to my care, will be briefly explained, touching upon the sources from which we get our material, the systems in vogue, the bulletins issued, the way in which the library becomes a clearing-house for information, a few of its typical problems, and lastly, its aims.

*Sources of Material.*—Our material is obtained chiefly through five channels: the purchase of special books or pamphlets to meet definite requests, through the mailing lists of outside concerns who send us their advertising literature from time to time, through the kindness of individual acquaintances at various points who desire to exchange results, from the chance notices appearing in the technical periodicals, which prompt us to initiate ourselves the getting of the information in question, and from the calls of clients and salesmen who may leave with us at their visits information of one kind or another. These are outside sources. The material produced within our own business of course comes to the library through the regular office routine.

*Classification.*—All of this material then, on its receipt, falls into one of the following six grand groups: books, pamphlets, trade catalogues, special data, periodicals, and the museum collection.

*Books.*—The books are classified by the Dewey Decimal System, which has long ago proved its claims in the public libraries. It serves our purposes very well indeed, and maintains uniformity with the best prevailing library practice in the majority of public libraries. By its use, like books stand together on the shelves, and those related stand closely by. It permits of perfect intercalation of new material upon the shelves in proper order. Supplementing the Dewey subject number, each book has its Cutters' author number. We use the Kate E. Sanborn arrangement of C. A. Sutters' alphabetic order table for assigning these numbers. All of our books are entered in an accession book on their reception, thus keeping accurate data on each volume.

*Pamphlets.*—Pamphlets receive treatment similar to that of the books as far as their numbering goes, but in order to keep this material in a distinct class by itself, the small letter (*p*) is used before the classification number. The pamphlets are then placed in regular pamphlet boxes on the shelves.

*Trade Catalogues.*—Trade catalogues receive a somewhat different treatment. This is the most objectionable class of material entering the library, owing to its entire lack of uniformity. We have found the best practical treatment to be a shelf arrangement, in which all the small material is enclosed in envelopes ( $9\frac{5}{8}'' \times 11\frac{3}{4}''$ , without flap, opening on the long side) and standing in one alphabet from (A) to (Z). To each company's catalogue is assigned a Cutter number, thus the catalogue of the Sturtevant Mill Company is S 936, which places it at one and the same time in a strictly alphabetical and numerical decimal order. This arrangement has the additional advantage of allowing those coming to the library seeking a definite concern's catalogue to go directly to the shelves, without the consultation of an index.

*Special Data.*—Our special data is a somewhat

miscellaneous class of material, made up of an accumulation of newspaper clippings, reviews of articles, results of personal interviews, special investigations, data culled from correspondence, and many other sources. The greater part of it is copied on correspondence size sheets, and placed in a vertical file. A small letter (*s*) preceding the number keeps this material distinctly in one class. The arrangement here is also by subject with the use of the decimal system.

*Periodicals.*—The class of periodicals is made up of a selected list of about fifty scientific and technical publications, both foreign and domestic. Many of these are purchased directly, while others are received with memberships in the different learned societies. Notable in this class of literature is a new type which is provoking some attention, the industrial publications. We may name a few, such as *The Stone & Webster Public Service Journal*, *Industrial Progress*, *Reactions*, *The Valve World* and *The General Electric Review*. For convenient reference all the periodicals are given symbols such as E N for *Engineering News*, E R J for *Electric Railway Journal*, P T J for *Paper Trade Journal*. Thus with the date of issue known, a certain reference can be easily and briefly made to any article. When the periodicals are later bound, as many of the better ones are, they of course leave this class and become books. As for the others, after clipping they are thrown away.

*Museum.*—The museum collection is made up of a large assortment of samples acquired from various points, clients, etc., for example, fibrous materials, mineral matter, special papers, artificial silks, standardized steels and irons, paper-making chemicals, electric railway materials, etc. To each individual sample we give a consecutive number, preceded by a small letter (*m*), which serves to keep this material in one group by itself. The material is filed in glass cabinets, where it is on constant exhibition, and proves, at least to our visitors, a source of lively interest.

*Color Scheme.*—In the actual handling of this material a color scheme is used. White tags are placed on the books, salmon on the pamphlets, blue on the catalogues, yellow on the special data, green on the periodicals, and cherry on the museum material. This is found to be helpful in the work, always aiding the eye in the rapid classification of material, and preventing often the return of material to the wrong place.

*Accessioning.*—Now as to the processes through which this bulk of material passes. Everything entering for permanent file is first accessioned, then catalogued and filed. The accessioning of the books has already been described; the other classes are accessioned on sheets kept for one week only, from which the information is later transferred to the weekly



bulletin, which will be described below. This does not apply to the periodicals which are checked upon a special card system as they are received, nor to the museum articles, which are not accessioned.

*Cataloguing.*—The classifying takes place next, which is followed as soon as finished by the indexing. Author, title and subject cards are made out in nearly every case, and often several subject cards. The cards completed, the materials go to their respective files, and the cards to the library index.

*Card Catalogue.*—This index is one large dictionary catalogue from (A) to (Z), and now numbers between thirty and forty thousand cards. These are all standard 3" x 5" library cards, and the entire index is liberally supplied with guides for the searcher. After locating the proper material wanted in the index, the nature of the call number on the card will always indicate the group in which the material itself will be found. This has already been explained in earlier paragraphs upon the different groups of material, by the use of the small letters (*s*), (*p*), (*m*), etc., as symbols in the call numbers. A distinctive feature of filing cards with us is the placing of them first in their proper places, without the removal of the rods from the drawers. A second party then goes through the cabinet, verifying them and dropping them into their permanent arrangement.

*Charging.*—The charging system carries out the color scheme. We have a small tray with the necessary compartments, in which narrow slips are used for keeping records of the material out of its regular place. White slips receive the book charges, salmon the pamphlet, blue the catalogue, and so on. On each slip is written the call number of the material, the initials of the borrower, and the date on which the loan is made. All material which is returned during the day is kept together in one place, and is returned to the files the first thing the following morning, the charge slips being removed at the same time from the charging tray.

*Bulletins.*—So much for the systems in vogue in our library. These are laid out with the idea that they may be almost automatic after those operating them have once learned them. But we now approach a more interesting side of the work. Every Monday morning we issue a bulletin which covers all the accessions of the previous week in classified shape, so that all the important heads of departments may at least keep up to date with what the library is doing. This bulletin idea is capable of much greater expansion, and as time goes on, we hope to make much more of it. It should contain suggestions, possible openings for increasing the business, perhaps a selected list of the more suggestive articles appearing in the press for the week, and so on. With sufficient time to devote to this purpose one can scarcely prescribe a limit to its possible development.

*Correspondence.*—For indexing purposes all of the correspondence of the various departments of our laboratory goes to the library before being filed. This is the regular channel through which all mail must go, and nothing is filed until noted by the library with its library stamp. This enables the library to pick out and index such useful bits of information as would otherwise be lost sight of.

*Library a Clearing-House.*—The library is the clearing-house for much of the information in our laboratory. Every second day the periodicals which have once been distributed among the staff come back by way of the mail baskets to the library, and are recharged and again distributed to a new group of readers. This system insures their receiving attention, for the readers know that the periodicals will be taken away whether read or not, when the time is up, and passed on to others. In another way the library acts as a clearing-house. If the Paper and Pulp Department brings us a request for information which we know is common knowledge in the Fuel Department, why should we not exercise our ingenuity in bringing the proper parties together? Again, if the Fuel Department works out successfully a problem which we know would help the Electric Railway Department, and the data is filed with us, why should we not call it to the latter's attention? You will readily see the effect this will have upon the general *esprit de corps* of the laboratory.

*Problems Encountered.*—Let us now look at a few of our typical problems: What are we asked to solve, and what form do these requests take? We have a form called our "Inquiry Blanks," printed on paper of a distinctive color. A pad of these blanks lies on nearly every desk in the various departments about the laboratory. When a request for information comes in or arises in any department, one of these forms is filled out and sent to the library, where it becomes our duty to provide an answer at the earliest possible moment. These slips are numbered consecutively as received, and after going to the accounting department for the distribution of their time charges, are returned to the library and kept in consecutive order. They serve thereafter as memoranda from which the answers can be readily found in case the inquiries are duplicated later from other sources, for each slip is filled out with the sources from which any information has come. As to the questions themselves, a few typical ones may be cited:

"Who are the principal manufacturers or dealers in copper sulphate?"

"What patents have been taken out on the removal of caffeine from coffee?"

"What is the procedure for anesthetizing plants?"

"Please give me a list of articles, with reprints and extracts, published during the past several years on Vanadium and Tungsten Steel."

"Who manufactures waterproof paper?"

"What is the practice in the use of the titer test as applied to red oil?"

"What is the present address of J. E. Teeple, of New York?"

"What is the price of and who sells the Hoskins' Electric Furnace?"

"Please find in a recent number of *Power* an article on the Westinghouse Gas Producer."

"What is the so-called New York-Liverpool test for soda ash?"

As you will readily see, these questions are of a most varied sort, and require a wide familiarity with the contents of the library, for we never know what may be asked next. We must ever keep before us the entire resources of the collection, and trust largely to our ingenuity and coöperation of all the laboratory members in finding satisfactory replies to these inquiries.

*Aims of the Library.*—This brings us to the aims of our library: Its first purpose must be to keep apace with the growing business of the laboratory and build up its resources in the most valuable way to handle the work. But this is not enough. We should be so keen to the situation as to try to sense the advance direction and movement of the business, and aim to build up our collection to meet the needs as they appear. Not only this, we must bear in mind the matters of vital interest to individuals. One man wants us to note for him everything we see on fibers, another would have us watching for articles on new steels, another for anything coming from the pen of a certain writer. All of these must be kept constantly in mind. But with these duties, which emanate from without, we should not be satisfied. It is for us to call also to the attention of those whom we may think will be interested such new developments, processes, inventions, treatises, and so forth, as make their appearance, for we are indeed privileged above the others in seeing so much that is diversified each day. With this privilege must go the added responsibility. Furthermore, we aim to keep in coöperative touch with other similar small libraries, as well as with the larger libraries, such as the Boston Public Library, the Library of the Mass. Inst. of Technology, and other institutional libraries, knowing that often we must go to those sources as a last resort when our own facilities have been exhausted. A sign of real progress in the general library field which has attracted our earnest attention of late is the formation of the Special Libraries Association, which hopes to unite the interests of all small special libraries, and to be of suggestive value to them in the solution of their varied and peculiar problems. We aim to keep in close touch with this movement.

*Conclusion.*—In conclusion, the library as an ad-

junct to the industrial laboratory may be said to be an actual necessity as soon as the laboratory has come to any size, and has an accumulated history. It facilitates the working of the organization, safeguards its resources, assists its specialists in their daily work, and makes for general efficiency. If it fully meets its purposes, it smooths the way and acts as a lubricant to the wheels of the laboratory progress, encouraging and building up the office coöperation, and enlivening the *esprit de corps* among its members. The library must become "a weapon of business," as has been aptly said before,<sup>1</sup> rather than a mere storehouse for books, if it is to be a real living and necessary adjunct to the industrial laboratory, and right here very much depends upon the missionary spirit of its staff.

BOSTON, MASS.,  
Dec. 30 1909.

## SCIENTIFIC PREPARATION AND APPLICATION OF PAINT.

By G. W. THOMPSON  
Received January 10, 1910.

The object of this paper is to discuss, abstractly, certain questions which arise in connection with the manufacture and use of paint. It is our purpose to see how far science will be able to help us and what the limits are, if such exist, to science as applied to the preparation and application of paint. Our purpose is to differentiate between science proper and that species of pseudo-science which is something in the nature of quackery. It is too common a practice in the arts to label a given product as "scientifically prepared," on the assumption that the popular mind will purchase it with avidity and with resulting large profit to the manufacturer.

We are glad to admit that imitation is the sincerest form of flattery. Unfortunately, this form of flattery does not help science, but, on the contrary, tends to put it in disrepute. As a general proposition, scientists should condemn the misuse of the name of "science" and should not be parties to it. This does not mean that science should not be popularized. There is no scientific proposition or problem but has its human side. The work of Faraday, Tyndall, and Huxley in the popularization of science are monumental examples that we should pattern after. Their methods, particularly, deserve study and imitation. We think that with them no false conclusion could possibly have been reached, because each conclusion was reached after careful logical thought, each premise was carefully examined before it was used and all its limitations noted, and when a final conclusion was reached, all the limitations of that conclusion were also stated.

<sup>1</sup> From a paper entitled "The Library and the Business Man," by G. W. Lee, presented at the 29th annual meeting of the American Library Association.

The scientific study of any subject involves the following steps:

*First:* The accumulation of facts and their careful study, so that there may be no question that the facts are reliable and safe within their limitations.

*Second:* The description of these facts, which description must be accurate, careful and not subject to more than one interpretation. Proper words must be used in this description and their definitions must be clear and accurate.

*Third:* The study of the interrelations of these facts and the development of such numerical values for these relations as may be found to exist.

*Fourth:* By the comparison of all the facts we may reach the condition where a hypothesis may be justifiable, for the purpose of explaining the interrelations of facts. There is no justification for the development of a hypothesis until sufficient facts are available. In proportion as a hypothesis connects facts, so far is it desirable, and, while it may not explain all facts, it should not be contrary to any fact.

The development of a hypothesis involves the use of the imagination, and, in so far as the use of the imagination is confined to the development of a hypothesis and is not allowed to color facts or dictate conception of laws, it performs a useful function.

*Fifth:* Laws may be developed by the classification and the organization of facts. Hypotheses may help in the discovery of laws, but hypotheses themselves must never be confused with laws. A law is something about which there is no exception. It should, if properly stated, rest on a firm foundation of all known facts. Too apt are we to use the word *law* loosely and improperly; such misuse of the word *law* is unscientific and cannot be too much condemned.

To the scientific study of paint, no one has contributed a greater fund of information and valuable suggestions than is to be found collectively in the classical articles by the late Dr. C. B. Dudley, which appeared in the *Railroad Engineering Journal* a score of years ago. These articles of Dr. Dudley are worthy of reproduction and study, and to every student of paints they should be an inspiration. The death of Dr. Dudley is a loss irreparable to the student of applied science.

*Facts and Conclusions.*—We have outlined the scope involved in the scientific study of any subject. All facts are contributive to science, so that the accumulation of facts is a scientific operation or step. It is proper, therefore, to refer to any classified accumulation of facts as scientific, and the more carefully these facts are classified, defined and described, the more scientific their accumulation is; but, when one attempts to apply these facts and to draw conclusions from them, then the operation is scientific only when all of the known facts are considered and the conclusions represent a complete and unbroken

chain of reasoning, without any lapses or assumptions either of facts or relation.

We hear a great deal about paints "scientifically prepared," without evidence being presented that these paints rest upon scientific foundations, properly so-called. We are told, for instance, that the best paint should have the minimum of voids in so far as its pigment is concerned, and then we are told that a certain paint or a certain group of paints has been scientifically prepared, without evidence being offered that these paints, in so far as the pigment is concerned, do have minimum of voids. This is not right. No conclusion should be based upon one fact only and no assumption should be made as to law or theory, but each should rest upon all available, known and applicable facts; and, if there is any gap which can be supplied by experiment, that experiment should be made so as to complete the links of available evidence.

Undoubtedly, science does contribute and assist in all manufacture of paint, gives information and facts that are enlightening and helpful to the manufacturer; but, to call the manufacture of paints scientific, simply because science furnishes facts, is very much like the use of the word electric in connection with carpet cleaning where electricity only is used for power. In both cases, there is a tendency to deceive. In the manufacture of a given paint, one scientific fact may be utilized and a hundred scientific facts may be ignored, and my contention is that no one is justified in describing a paint as scientifically prepared unless all known facts and relations are considered in its preparation. Commercially, in my opinion, this is impracticable. A small amount of paint could be prepared in this way, but there would have to be considered the surface to be painted, the weather conditions in which the painting was to be done and the personal equation of the painter together with all the variables peculiar to the pigment and vehicle used.

I would not, for one moment, be considered as condemning the application of science to paint manufacture; there is no limit to the usefulness of science in this respect. We are learning more and more every day, and the paint industry is advancing by leaps and bounds with the knowledge that science is furnishing it. As illustrating my views, I would mention that, at a meeting of the American Society for Testing Materials in 1907, I suggested that a test should be made to determine the effect of pigment upon the corrosion of iron and steel. This test involved the agitation and aeration of water containing a given pigment in contact with a weighed piece of steel. A number of tests were to run at once, so that the agitation, aeration, etc., should be uniform. The tests, which were made at my suggestion, indicated that certain pigments accelerated corrosion,



while other pigments retarded or inhibited corrosion. This test was suggested as giving valuable information which, taken in conjunction with other information, would help in the designing of a suitable paint for iron and steel. In order to determine the value of this test, a number of painting tests were prepared and exposed, using different pigments, but the same oil, and with all the paints spread at a standard rate. It was thought that, while a pigment might be an accelerator of corrosion in water, it might act differently in linseed oil. The reports of the inspection of the painting tests so far published give us no information as to whether the laboratory water-test is reliable or not. Individually, I am unwilling to express opinion on this point, and will not anticipate the report of the Inspection Committee.

But, two alternatives are before us:

*First:* If the painting tests confirm the laboratory water-tests, then further work will have to be done to determine to what extent an accelerating effect possessed by one pigment can be overcome by admixture with another pigment; also, if a pigment accelerates corrosion, could not special methods of preparation be devised which would overcome this accelerating effect?

*Second:* If the paint tests do not confirm the laboratory water-tests, investigation should be undertaken to find the cause of this disagreement.

Broadly speaking, a pigment may be an accelerator of corrosion and have other valuable properties which will commend it for protective coatings; and, on the other hand, a pigment may be a good retarder of corrosion but have other objectionable qualities which will condemn its use in protective paints.

Also, a pigment may give a paint coating that is relatively impermeable, and so prevent corrosion, but produce a paint coating that is not reasonably permanent. In such a case, initial impermeability is of small value as compared with lack of permanence.

These illustrations are presented simply to bring out the point we have in mind that all the qualities of a pigment must be taken into consideration when it is used or advocated scientifically.

We cannot discuss in this paper all of the phases of paint manufacture, nor can we consider all of the properties which a pigment might possess, but which must be considered when it is to be used in the preparation of paint. Chemists are more apt to consider pigments from the chemical, rather than from the physical, side. It is a common practice for them to analyze a given pigment; then to find from the analysis that the composition accords with what they believe to be a standard composition and then to endorse that pigment as a valuable one. The neglect of the study of the physical properties of pigments has been the cause of a great waste of money, time

and effort in paint manufacture. Analysis is perhaps the most important means of enlightenment that the paint manufacturer possesses, but his examination must not stop here. Too little study has been given to the size and shape of pigment particles and their physical relation to the vehicle used.

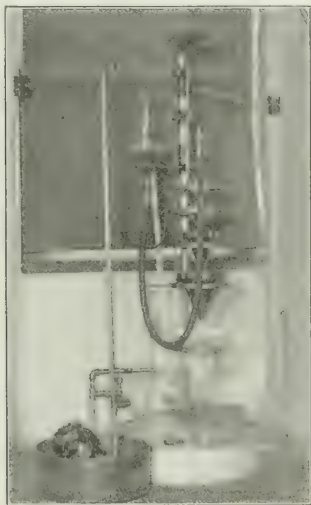
*Size and Shape of Pigment Particles.*—The use of the words *fine* and *coarse*, with reference to pigments, is often misleading. We would define *fineness* as a word that expresses the relative number of particles in an absolute unit of volume. If the unit of volume is taken as one cubic centimeter then the word *fineness* corresponds to the number of particles in "S" grams of the pigment, where "S" equals the specific gravity of the pigment. Unfortunately, there have been no measurements of pigment particles which will give us their relative fineness in these terms. We should have this information if we would classify and describe pigments properly, according to their fineness. Practically, a pigment is not considered fine enough when it contains any gritty particles, which grit will ordinarily be caught on a fine silk bolting-cloth; but, on the other hand, a pigment may be too fine for use by itself in certain paints because it may not contain the proper proportion of relatively coarse particles. Now, if we had some method of determining the number of particles in an absolute unit of volume, it would be comparatively easy to design a paint by the admixture of pigments that would contain any desired number of particles to the absolute unit volume. Microscopic examination has not been sufficiently accurate for this purpose, for the reason that microscopic measurements of fine particles, as a rule, only take in two dimensions; and, as, with the exception of precipitated crystalline pigments, the particles are not symmetrical, it seems almost impossible to determine the absolute volume of a given unsymmetrical pigment particle. When a pigment is made up of particles of different sizes, the difficulty becomes even greater.

The finer the pigment is, the greater its oil-taking power is; consequently, this oil-taking power is an indication of fineness. We do not know, however, that it is more than an indication, for the shape of the particles and the surface they expose to contact with the oil are also factors in the oil-taking power of the pigment. In testing for the oil-taking power of a pigment, it is desirable that, as far as it is possible, any chemical reaction between the pigment and the oil should be eliminated. Mineral oil is, relatively speaking, inert toward most pigments and is probably the most suitable oil to use to determine the oil-taking power of a pigment.

There is no subject connected with the paint industry which deserves more scientific investigation than this one of the oil-taking power of pigments. Formulae should be developed to show the relation be-

tween the size of particles and their oil-taking power, although it may be necessary in these formulae to have constants that will represent the specific surface tension which exists between the specific particles being tested and the oil used.

It has been my endeavor during the last two years to develop a suitable classification apparatus which, in the case of simple pigments composed of particles of varying size, will classify these particles according to size. The apparatus which I have devised is shown in the accompanying photograph and consists of inverted cones of four different sizes placed one above the other. The pigment to be tested is placed in the top cone, and kerosene at a constant head, and consequently at a known speed, flows through a glass tube into the bottom of this top cone; as it overflows, it passes through a funnel into the bottom of cone No.

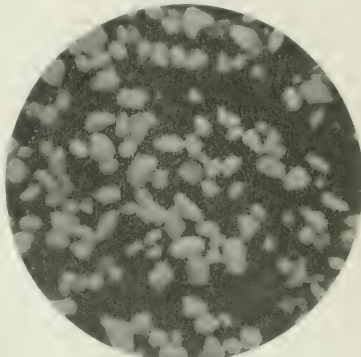


2, and so on, from cone to cone. These cones vary so in size that with a given pigment, if the diameter of the smallest spherical particle in cone No. 1 is "A," then the diameter of the smallest spherical particle in cone No. 2 would be  $"A" \div 4$ , in cone No. 3  $"A" \div 16$ , and in cone No. 4  $"A" \div 64$ .

I show you here photomicrographs of a certain pigment classified in this way. The classification should, of course, be carried further, and in time we hope to have an apparatus built that will carry this classification to its final limit.

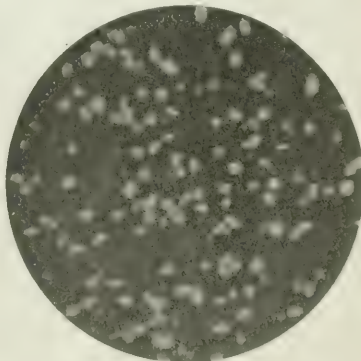
The question is, can we say that a certain pigment or mixture of pigments is better than others, as the result of our scientific knowledge of the size, shape and number of particles in the absolute unit of volume? Have we any well-established laws to guide us? My opinion is that, while we have a number of theories,

we have no laws. Robert Job has told us that samples of a certain pigment of a given composition, but varying in fineness, had a durability in proportion to fineness. Facts of this kind are valuable, but, unfortunately, unless the conclusion reached is carefully limited by the facts available, one may readily



Cone No. 1

reason to a point where infinite fineness would be advocated and with it infinite unworkability. In other words, if the information were available, it would probably be found that the different samples of the same pigment referred to varied only in the proportion in which the various sized particles were present. It would appear, therefore, that the art of paint-making, in order to be scientific, should involve the establishment of rules and formulae governing the proportions of different sized particles in a pigment. Much has been written in advocacy of three sizes of

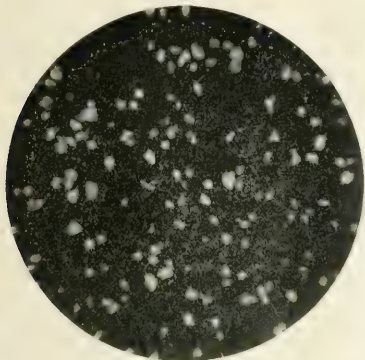


Cone No. 2

particles in a pigment, but why the mystic three was adopted it is hard to understand.

Also, much has been said about the law of minimum voids, but there is no law of minimum voids, although there may be a hypothesis. Certainly, there is no law showing that three-size particles give

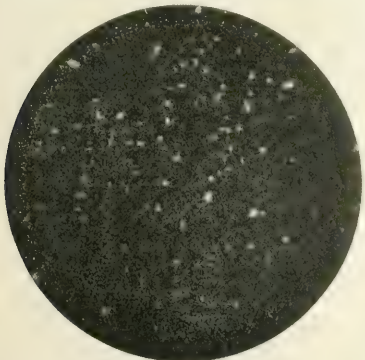
minimum voids. There is, practically, no published work showing how a minimum of voids can be obtained. We know that more than one size of particles is to be desired, but we do not know that we should stop at one, two, three or four, or at any number of sizes. I might personally advance the theory,



Cone No. 3

as I have done, that an infinite variety in size of particles, in general, produces a pigment with the minimum of voids, but even that theory remains to be developed.

The more one studies the question of voids, the more complicated the question becomes, and it would appear impossible to predict whether any given mixture of pigments would result in a reduction of voids as compared with the voids in either of the pigments used. This would appear to be due to the fact that each pigment has its own peculiar and specific form; and it is probable that, with some of the finer pig-

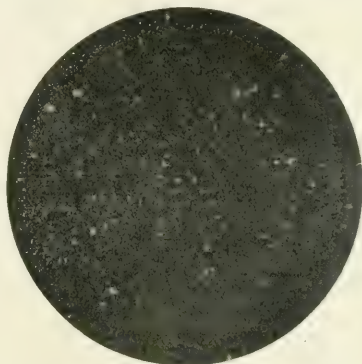


Cone No. 4.

ments, there is a different surface relation between the particles than exists with the coarser pigments. It would also appear possible that something akin to the colloidal condition may exist with pigments in their relation to vehicles, and even to the air with which, in their dry state, they are surrounded.

The coarser pigments may be crystalline or may have a conchoidal fracture. Precipitated pigments are usually crystalline and the particles are usually very nearly of the same size. Fire process pigments are usually very fine and would appear to be without definite form, indicating that the air or gases in which they are formed do not act as a crystallizing medium; that is, that the air is not a solvent for these pigments during their formation. The method of grinding affects the shape and size of particles. Air-ground pigments usually have more of a tooth than water-ground pigments; that is to say, water-ground pigments are usually softer than air-ground. Another peculiarity of pigments is that some tend to flocculate more than others, making their microscopical examination exceedingly difficult and their oil-taking power variable. We refer to these facts to illustrate the impossibility of figuring *à priori* what the physical relation of a mixture of pigments will be.

The question of voids is still further complicated



Portion No. 5.

by the vehicle. Should voids be determined with the dry pigment, with the pigment ground in oil, or with the pigment thinned with turpentine? Obviously, if the pigment were to be tested dry for voids, some method should be used which would secure a representative sample and subject it to a uniform pressure. The question would then arise, What pressure should be used? The dry determination of voids cannot be accepted as a guide, unless it is shown to correspond in some way with the voids, using a paint vehicle. Now, it would appear that with a dry pressure-test, the specific gravity of a pigment would not affect its voids, while with an oil vehicle the voids would be affected by this specific gravity. In oil, the lighter pigments give a higher per cent. of voids and the heavier pigments a lower per cent. of voids.

In the actual practice of making prepared paints, it would appear that the paint manufacturer wants to increase the voids so as to minimize settling. If



the best paint is the paint with the smallest percentage of voids, then the paint manufacturer is working in the wrong direction in trying to obtain a paint which will stay best in suspension.

Much of the confusion which has arisen in connection with the discussion of voids has been due to a lack of definition of the word *voids*. Properly speaking, *voids* can only refer to the *space between solid particles*; and yet we are told by some that a linseed oil film contains voids. With concrete, etc., voids are defined as "the spaces throughout a mass of concrete, mortar or paste that are filled with air or water" (Taylor and Thompson's "Treatise on Concrete," 1907). If we are to include vehicles when dry as a part of the solid matter, we will get nowhere in our calculation of voids. If we are to include vehicles we might as well include air and water; so that, in every case, except in a vacuum, the percentage of voids would be zero. In order that we shall talk intelligently and rationally concerning voids in paints, we must confine the expression to the space throughout a mass of pigment or paint that is filled with air or vehicle; in other words, it must be confined to the space between the solid particles of pigment.

If we were to define a scientifically prepared paint, it would be somewhat as follows: The pigment and vehicle should be composed and proportioned of such materials as have been found by careful scientific research to give the best results on the specific surface to be painted, taking into consideration the exposure to which it is to be subjected and the personal equation of the man of men to apply it. In the preparation of such paint, no factor or element should be omitted, unless it can be demonstrated that that factor or element is negligible. We may well doubt that such a paint has ever been prepared, and we are inclined to add that such a paint will never be prepared, for the reason that the personal equation of the man who applies the paint is a dominating factor in obtaining good results. In fact, it appears to me that the application of paint is an art, and not a science, and I have the profoundest respect for the competent painter who knows how to use his materials and blend them so as to obtain desired results. His is a laboratory work upon a large scale and his knowledge is accumulative, and every painting job contributes to his stock of knowledge. From the competent painter must ultimately be received the commendation or condemnation of the theories which students of paints may propound.

In conclusion, permit me to repeat that all knowledge is within the scope of scientists and contributes to the development of science, and every piece of information that can be obtained regarding any given problem should be utilized by scientists to its full worth. What we make a plea for is, *genuine scientific thought* that will be conservative and will not

jump at conclusions, that will not lay down laws which have no foundation, and that will not use terms loosely and ambiguously. The aim of science should be usefulness. Science should clarify the mind, and not befog it. To the end that paint manufacturers may become truly scientific I commend this paper.

### A CONVENIENT METHOD OF REFRIGERATION FOR ANALYTICAL AND INDUSTRIAL INVESTIGATIONS AT LOW TEMPERATURES ( $-75^{\circ}\text{C.}$ ).<sup>1</sup>

By JAMES O. HANDY.

Received January 10, 1910.

The method I am about to describe may be familiar in principle to most of you, but I believe that its convenience is not generally appreciated, nor are the little details of manipulation so well known as they should be.

The usefulness of a ready means of producing and holding low temperatures is readily granted. It is especially useful to physicists and to chemists, and is doubtless more familiar to the former than to the latter.

In chemical work, refrigeration has been found of special use in ways of which the following are illustrations:

(a) *Paraffine Wax Determinations in Petroleum or Its Distillates*.—Refrigeration will, I believe, eventually be useful in separation of waxes, resins and any other bodies which will crystallize or precipitate at varying concentrations from solution in volatile solvents under the influence of cold.

(b) *Condensation of the Most Volatile Distillates from Petroleum*.—Certain of these low-boiling hydrocarbons are found in gaseous form in natural gas. As they are not always present, refrigeration is a convenient means of testing the gas from different fields.

(c) *Freezing tests of oils* to ascertain whether they will do the work expected of them if they are subjected to the influence of winter temperatures in the northwestern United States or Canada ( $-40^{\circ}\text{C.}$  or lower).

This refers to oils used for lubrication, but is of most vital service in testing oils for use in railway signal apparatus where certainty of operation is necessary if accidents are to be avoided.

(d) Rectification of chloroform in process of manufacture by the use of low temperature.

(e) Purification of acetylene by treatment with sulphuric acid at  $-50^{\circ}\text{C.}$  At this temperature only the impurities are acted upon by the acid.<sup>2</sup>

This discovery makes it highly probable that sim-

<sup>1</sup> A paper read at the Boston meeting of the American Chemical Society, December 28, 1909, by James Otis Handy, Chief Chemist of the Pittsburgh Testing Laboratory.

<sup>2</sup> Ewing, "The Mechanical Production of Cold," Cambridge University Press, 1908, p. 134.

ilar methods will be applied to difficult analytical and industrial separations or purification processes. Chemical affinities which at ordinary temperatures act as stumbling blocks to investigators and manufacturers may be much changed, or even entirely reversed at low temperatures.

For convenient production of temperatures down to  $-15^{\circ}$  C. in laboratory investigations, ice and salt mixtures have been the commonest means. By use of snow and salt or calcium chloride solutions slightly lower temperatures have been obtained, but various difficulties are encountered, and the method is no longer properly described as convenient.

Snow and 50 per cent. sulphuric acid, equal parts, are said to produce a temperature of  $-50^{\circ}$  C.

One part snow and three parts of crushed calcium chloride are said to produce  $-58^{\circ}$  C.

These figures are interesting, but the methods would not, in the author's opinion, be convenient. We have not been able to verify them. Perfect insulation of the containing vessel would be necessary to even approximate the temperatures mentioned, and the low points would be only transitory.

Liquefied gases, which are commercially available, are supplanting the cruder methods of refrigeration. Of these liquid gases, liquid air can be had at about \$4.00 per liter if the purchaser is willing to assume the risk of breakage of a special vacuum container valued at \$50.00. The loss by evaporation from such a vacuum vessel is stated to be from 5 to 15 per cent. per 24 hours, according to the size of the vessel and the amount of agitation it receives. Evidently consumers at a distance from the factory would be subject to considerable expense and frequent disappointment. If extremely low temperature (such as  $-190^{\circ}$  C.) is needed, liquid air is the only practicable means to use.

Ammonia is useful for industrial refrigeration when used by alternate compression and expansion in a refrigerating system. It is rarely used for temperatures much below  $-10^{\circ}$  C., although the boiling point of liquid ammonia is  $-39^{\circ}$  C. at atmospheric pressure.

The use of ammonia in small-scale laboratory investigations in which the ammonia is allowed to escape into the air is manifestly undesirable.

For researches at temperatures down to  $-78^{\circ}$  C. liquid carbon dioxide is the most convenient refrigerant. It can be purchased in nearly every city or town, and its cost is approximately ten cents per pound. Its commonest container is a steel drum built to withstand internal pressure of over 3700 lbs. per square inch. Safety valves are arranged to release at 2100 lbs. The pressure in the charged drum is 1150 to 1350 lbs. per square inch, according to the temperature outside.

The way to use carbon dioxide as a refrigerant

satisfactorily is not to allow the liquid to escape as gas around the object to be chilled.

Very low efficiency is obtained in this way as the refrigerating effect is not concentrated but diffused. Furthermore, the exit valve is soon clogged with solid carbon dioxide or snow.

This snow is the proper basis for satisfactory refrigeration, although it is much more efficient if used in solution in a solvent of low solidifying point.

In order to prepare the  $\text{CO}_2$  snow economically, we have used the method of allowing the liquid to discharge through canvas bags tied over the outlet. A piece of rubber tubing of the length of the bags, while not necessary, diminishes the waste by hastening the deposition of the first layer of  $\text{CO}_2$  snow, which acts as a nucleus or condenser for the rest.

We have obtained a maximum yield of 29 per cent. of  $\text{CO}_2$  snow by this method. About one pound of snow was obtained in less than two minutes (380 grams in  $1\frac{1}{2}$  min.).

Doubtless the yield of snow could be greatly increased if larger amounts were made in less crude apparatus.

The  $\text{CO}_2$  snow is, as its name implies, very much like slightly moist snow in appearance and consistency.

It can be consolidated or further subdivided by the pressure of the fingers. It keeps well for short periods in the canvas bags wrapped in a loose towel. The rate of evaporation of a 130-gram lot under these conditions, at ordinary temperature, was 53 grams per hour. In a cotton-stoppered one-quart size vacuum vessel (Thermos bottle) the rate of evaporation of the  $\text{CO}_2$  snow was only 8 grams per hour, when 100 grams were present, and the snow remained dry and loose enough to pour out after several hours had elapsed.

$\text{CO}_2$  snow can be handled easily because it absorbs heat very slowly from objects with which it comes in contact. This fact diminishes its value as a convenient refrigerant.

If, however,  $\text{CO}_2$  snow is dissolved in acetone or other volatile solvent of low freezing point, its rapid action as a refrigerant becomes remarkable, and it is at the same time even more conveniently handled and applied than is the  $\text{CO}_2$  snow itself. It will flow freely into cooling jackets where the snow could not go.

The relative efficiency of  $\text{CO}_2$ -acetone-snow and the snow alone is shown by the fact that 350 grams of alcohol were cooled through  $23^{\circ}$  C. in 2 min. by 180 grams of  $\text{CO}_2$  acetone containing approximately 30 per cent., or 54 grams, of  $\text{CO}_2$  snow, while a much greater weight of  $\text{CO}_2$  snow (120 grams), used by itself, only cooled the same amount of alcohol  $6^{\circ}$  C. in two minutes.

Hardin—in his book "Liquefaction of Gases,"

MacMillan & Co., 1899—says that liquid  $\text{CO}_2$  is soluble in all proportions in alcohol, ether, naphtha, turpentine and  $\text{CS}_2$ .

We believe that D'Arsonval,<sup>1</sup> a French investigator writing at the request of M. Henri Moissan, first called general attention to the efficiency for experimental refrigeration of solutions of  $\text{CO}_2$  or  $\text{C}_2\text{H}_2$  in acetone.

Liquid acetylene forms snow which also dissolves freely in acetone, and yields a solution which reaches  $-112^\circ \text{C}$ . Solutions of  $\text{CO}_2$  snow in acetone can be made to reach this temperature if placed under vacuum, or if evaporation is hastened by the passage of refrigerated air. Similarly the temperature of acetylene snow in acetone can be further reduced.

As an illustration of the rapidity of the action of the  $\text{CO}_2$  acetone, it caused 430 grams of mercury to freeze solid in 2 min. and 40 seconds. We placed an open beaker containing it in a larger open beaker of the refrigerant. Hg freezes at  $-39^\circ \text{C}$ . The refrigerant weighed 193 grams and contained about 35 per cent.  $\text{CO}_2$ . Its temperature rose from  $-63^\circ$  to  $-43^\circ$  during the freezing of the mercury.

The approximate amounts of  $\text{CO}_2$  snow and acetone necessary to produce certain temperatures are as follows:

150 gm. acetone at  $23^\circ \text{C}$ . + 6 gm.  $\text{CO}_2$  =  $-5^\circ \text{C}$ .  
   + 11 gm.  $\text{CO}_2$  =  $-20^\circ \text{C}$ .  
   + 24 gm.  $\text{CO}_2$  =  $-38^\circ \text{C}$ .  
   + 45 gm.  $\text{CO}_2$  =  $-54^\circ \text{C}$ .  
   + 77 gm.  $\text{CO}_2$  =  $-61^\circ \text{C}$ .  
    $\text{CO}_2$  in excess =  $-78^\circ \text{C}$ .

114 gm. petrole ether of  $86^\circ \text{B}$ . at  $22^\circ \text{C}$ .:

  + 5 gm.  $\text{CO}_2$  =  $-22^\circ \text{C}$ .  
   + 10 gm.  $\text{CO}_2$  =  $-36^\circ \text{C}$ .  
   + 15 gm.  $\text{CO}_2$  =  $-55^\circ \text{C}$ .  
   + 30 gm.  $\text{CO}_2$  =  $-69^\circ \text{C}$ .

It appears from this that petrole ether reaches a low temperature more quickly. This is probably because it is more volatile. It foams more when the snow is added to it. Acetone, however, is, as D'Arsonval says, the best of the solvents for general use. Most of the others give deposits which would clog cooling jackets.

If absolute freedom from fire risk is desired,  $\text{CCl}_4$  or  $\text{CHCl}_3$  and  $\text{CO}_2$  can be used for a limited range.

I wish to give credit to my assistants, Messrs. Craver, Johnson, Thompson and Burris, for their work with me in this matter.

#### SUMMARY.

(1)  $\text{CO}_2$  snow dissolved in acetone or other volatile solvent will quickly chill substances to  $-75^\circ \text{C}$ . or to any intermediate temperature (D'Arsonval).

(2) The snow is prepared by allowing the liquid

$\text{CO}_2$  to blow off through canvas or flannel bags, according to the well-known method.

(3) This convenient method of refrigeration is of immediate use for many investigations, and is likely to be of service for purification of chemical products and for analytical separations.

#### ASSAY OF MEDICINAL PLASTERS.

By FREDERICK B. KILMER.

Received July 31, 1909.

Comparatively little literature has appeared in scientific publications in respect to the analysis of assay of medicinal plasters made with an India rubber base.

The enactment of the Federal Food and Drugs Act and the enactment of similar laws in the various states has brought the subject to the attention of the pharmaceutical chemist, and at the present time the subject is one of moment to both the medical and pharmaceutical professions.

Prior to the issuance of the last revision of the pharmacopoeia no authoritative process of assay of any medicinal plaster appeared in that work. In this revision a process was given for the assay for mydriatic alkaloids in belladonna plasters made with rubber base. Those who have given attention to the subject will no doubt agree with the statement that has been made, that it is a very difficult matter to assay some kinds of medicinal plasters made with a rubber base. It is a well-known fact that for some such plasters no method is known for the assay of the drugs contained therein, for the reason that the drug used has no alkaloid or no inorganic substance capable of definite measurement.

In other varieties of these plasters the presence in the rubber base of resinous or other matters is such as to confuse the results and make them of doubtful value. In the laboratory of the writer considerable work has been done in the assay of this class of preparations, and in our work we possess some advantages over any outside laboratory, in that as the laboratory is connected with the manufacturing department, it is at once known exactly what has been put into a plaster, and it is only necessary to provide methods of assay that will give the results looked for. The methods and processes which I herewith present are simply those which have been worked out in the laboratory, namely as a check to manufacturing processes. They are presented for what they may be worth, with the hope that other workers may have an opportunity to try them and thus bring out information of value to those interested.

For belladonna plasters we used the assay method of the eighth revision of the United States Pharmacopoeia. This process, with some slight modifications, has been entirely satisfactory in our laboratory, where assays, running perhaps into thousands, have been performed. It has also had the benefit of an

<sup>1</sup> "Production and Maintenance of Low Temperatures," D'Arsonval in *Comptes rendus*, Vol. 133, 980 (1901).



extended check test, in that in this laboratory it is our practice to first assay the drug used in the manufacture of the plaster and then the solid extract made from the drug; the mass itself is made up of the assayed extract taken in an amount which will give in the finished product the desired percentage of alkaloid required in the plaster, and by this method of plaster assay the results have shown that in mixing several hundred pounds the assayed plaster corresponds with the calculated amount often to the second and third decimal.

*Salicylic Acid Plaster.*—The method which we use for the analysis of salicylic acid plaster is a colorimetric method with ferric chloride. The depth of color imparted to a ferric chloride solution by a measured amount of a solution of the plaster is compared with that of a measured quantity of a standard solution of salicylic acid of known strength. Colorimetric methods are always subject to some variations, chiefly, on account of errors of eyesight, as well as to the presence of resinous materials in rubber plaster masses; no other method has been found to be satisfactory and we have found that by careful manipulation, the color comparison method has given sufficiently satisfactory results.

*Plaster Solution.*—Weigh out accurately about 5 grams of the plaster cut into rather small strips. Place on the table two beakers of about 150 cc. capacity each. Designate them as No. 1 and No. 2. Place the weighed strips of plaster in No. 1. Add to it 50 cc. chloroform. Stir gently until all compound is removed from the plaster-cloth and in solution. Pour the sirupy solution into beaker No. 2. Add to this in No. 2 beaker 40 cc. ordinary 94 per cent. alcohol, stir thoroughly to precipitate and coagulate the rubber and allow it to stand. Pour off all possible of the liquid into a glass-stoppered, graduated 250 cc. flask. The rubber should be worked up into a compact mass so that no particles are carried over when the liquid is poured off, and all possible liquid should be pressed out of the mass with a glass rod.

To the plaster-cloth in beaker No. 1 add 25 cc. chloroform. Stir carefully and thoroughly until all remaining plaster-mass is dissolved from the cloth and sides of the beaker. Pour off again into beaker No. 2, which contains the precipitated rubber. Work up with a glass rod until all of the rubber mass is again in solution in the chloroform. Now reprecipitate the rubber from this solution with 20 cc. alcohol, working up with rod and pouring off as before, mixing the fluid with the first portion in the flask. Once again wash the cloth in beaker No. 1 with 25 cc. chloroform. Pour off into No. 2 beaker, dissolving again the rubber mass in it. Reprecipitate the rubber from it with 20 cc. alcohol as before, pour off and mix the decanted fluid with the other two portions in the flask which now contains all of the sali-

cyclic acid in solution. Fill the flask up to the 250 cc. mark with alcohol.

Remove the cloth, which should now be white and clean, from beaker No. 1, allow to dry spontaneously and weigh. Subtract its weight from the total weight of plaster used, thus ascertaining the weight of plaster compound taken for assay.

*Standard Salicylic Acid Solution.*—Weigh out exactly 0.5 gram pure salicylic acid and dissolve it in 50 per cent. alcohol. Transfer to a 500-cc. glass-stoppered, graduated flask, rinse out the vessel, in which the acid was dissolved, with repeated portions of 50 per cent. alcohol, adding each portion to the solution in the flask. Make up to the 500 cc. mark with 50 per cent. alcohol, shake thoroughly. 1 cc. of this solution contains 0.001 gram salicylic acid.

*Analysis by Color Comparison.*—For this work we use two large test tubes of similar internal diameter ( $1\frac{1}{4}$  inches by 6 inches long). Any pair of glass cylinders or tubes will suffice, but small diameter test tubes do not give sufficient thickness of solution to secure enough depth of color with transmitted light. Place these tubes side by side. In a beaker place 100 cc. distilled water, to which add one drop ferric chloride solution, U. S. P. Stir and pour into each of the test tubes 50 cc. of this. Designate them No. 1 and No. 2. Now add to No. 1 tube from burette sufficient of the standard salicylic acid solution to give a strong, clear, wine color. Stir with a glass rod after each addition of the acid solution. Multiply the number of cc. used by 0.001 which will give the weight in grams of salicylic acid used in tube No. 1—the standard. Now add to tube No. 2 from another burette sufficient of the plaster solution exactly to match the color obtained in tube No. 1. This plaster solution must be added a little at a time and the solution in the test tube well stirred with a glass rod after each addition. When the matching point is nearly reached it may be necessary to filter off the contents of test tube No. 2. Clean the tube and replace the fluid—proceeding thereafter to add the plaster solution, a drop at a time. The reason for doing this is on account of the small amount of resinous matter separated from the solution, which may cloud the mixture in No. 2 test tube and interfere with the color judgment. By closing one eye and observing the colors while holding the tubes side by side between the eye and a window, the colors can be matched very closely. It is obvious that the quantity of plaster solution used contains the same amount of salicylic acid as was used in tube No. 1. That quantity is already determined by means of the standard solution. Therefore 250 (total amount of plaster solution) divided by the number of cc. plaster solution used in tube No. 2 and the result multiplied by grams acid found to have been used in tube No. 1 gives the weight of acid in the plaster compound.

Multiply the weight of the salicylic acid found by 100 and divide the result by the weight of the plaster compound used. The result is the per cent. salicylic acid present.

This method has been used chiefly with plasters containing 20, 25, and 30 per cent. of salicylic acid. When very small percentages are present it will of course necessitate the addition of a much larger quantity of plaster solution to tube No. 2 in order to secure the same color as No. 1 tube and, consequently, the color of tube No. 2 will be unduly diluted. If by trial this is found to be the case, it will be necessary to prepare a weaker standard solution or else a more concentrated plaster solution. This matter can readily be determined by trial.

In making these assays it is well to make three of each and take the average. By doing this we have been able to get satisfactory results, the natural variations of color judgment balancing one another and the result being nearly correct in the average of the three determinations from one lot of plaster solution.

*Mercurial Plaster.*—The requirement of the U. S. P. is that it shall contain 30 per cent. metallic mercury.

*Method.*—Weigh out about 5 grams of the plaster, cut in rather small strips. Place in a beaker and add about 50 cc. benzol. Stir well for some time to soften and dissolve the compound. Pour off into a beaker of about 300 cc. capacity, allowing the cloth to remain in the first beaker. To the cloth in the first beaker add repeated portions of about 50 cc. benzol, stirring well and pouring off each time into the second beaker until the mixed solutions amount to about 200 cc. The clean cloth is now allowed to dry in the air, weighed, and its weight subtracted from the weight of the plaster taken. This gives the weight of the compound used.

The mixed solutions of the compound, measuring about 200 cc., are now well stirred and then allowed to stand covered, in a tall beaker, until the gray metallic mercury has settled to the bottom. This usually is accomplished in about twenty-four hours. Chloroform can be substituted for benzol in this dissolving operation, but benzol is used in our work on account of its relative lightness, because of which the mercury settles more quickly.

When the gray mercury has settled out pour off carefully the supernatant benzol, which contains the rubber and resins in solution. On account of the high gravity of the mercury the benzol can be decanted until nothing remains but a slime of mercury powder. To this add at once one or two cc. of aqua regia, warm it, stir and let stand. If all gray color is not removed in about an hour add another cc. of aqua regia, stir, warm and let stand again, repeating, if necessary, to dissolve all of the mercury. Use,

however, as little acid as possible so as to avoid all but a slight excess, for much excess will interfere with the subsequent precipitation of the mercury by means of  $H_2S$ . When the acid solution has lost all gray color, indicating the complete solution of the mercury, add about 50 cc. water. Stir, and filter through a paper filter containing a tuft of absorbent cotton. The cotton catches the flocculent particles of resinous matter and prevents stoppage of the filtration by clogging. Rinse out the beaker with repeated portions of water, which is poured through the filter. Continue until about 200 cc. filtrate are secured. Place this filtrate in an Erlenmeyer flask of ample capacity to pass  $H_2S$  through it until the mercury is all precipitated as black  $HgS$ . Let it settle a few minutes and filter at once through a weighed filter paper of fine texture, wash the precipitate on the filter with a little water, and dry at  $100^\circ C.$ , cool and weigh. Subtract weight of filter paper and calculate the resultant weight of the mercury sulphide to mercury, viz.:

$$232 : 200 = \text{wt. } HgS : x \text{ wt. mercury.}$$

The weight of mercury found multiplied by 100 and divided by the weight of the compound used gives per cent. mercury in the compound.

*Ammoniac and Mercury Plaster.*—The requirement of the U. S. P. is that it shall contain 18 per cent. metallic mercury.

Method of assay for mercury—same as with mercurial plaster.

*Strengthening Plaster.*—Assay for iron: weigh out accurately two pieces of plaster of about 5 grams each, cutting them side by side from the same piece in order that the relative amount of compound to cloth will be the same in each piece.

Dissolve off the compound from one of the pieces with repeated portions of chloroform until the cloth is clean. Allow the cloth to dry spontaneously and weigh it. Multiply its weight by 100 and divide by the total weight of plaster used. This gives the per cent. of cloth in the plaster, the figure so obtained to be used later.

The second piece of plaster of known exact weight is placed in small clippings in a porcelain crucible and ignited. Dissolve the residue in warm concentrated hydrochloric acid, dilute about 200 cc. with water and filter. Place in a porcelain dish, heat nearly to boiling and add ammonia in excess to precipitate the iron as  $Fe_2O_3 \cdot H_2O$ . Let settle, decant on to a paper filter of known low ash value, wash the precipitate with hot water and dry. This is now ignited in a weighed porcelain crucible with lid, the iron hydroxide being first carefully scraped from the filter and ignited alone in the crucible, and the paper containing only a little adherent hydroxide is ignited separately on the lid of the crucible. When the paper is completely reduced to ashes, the lid is placed

on the crucible and both are transferred to a desiccator to cool. When cooled, weigh and subtract the weight of the crucible and lid from the weight of the same with contents. This gives the weight of iron oxide ( $\text{Fe}_2\text{O}_3$ ) contained in the crucible.

This is calculated to metallic iron, *viz.*:

$$160 : 112 = \text{wt. Fe}_2\text{O}_3 : x \text{ wt. Fe.}$$

The percentage of cloth in the plaster has been determined as above in other piece of plaster, therefore the weight of the piece of plaster ignited is multiplied by the per cent. figure for cloth, determined in the other piece of plaster. The weight so found is subtracted from the weight of plaster ignited, which result is the weight of compound ignited.

The weight of Fe found, multiplied by 100 and divided by the weight of compound ignited, gives the per cent. Fe in the compound.

To Arthur W. Clark and Powell Hampton acknowledgment is due for work in the elaboration of these processes.

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## METHODS FOR TESTING COMMERCIAL, ANHYDROUS, LIQUID AMMONIA.

By W. D. RICHARDSON.

Received January 1, 1910.

The average refrigerating engineer is very critical of the quality of the anhydrous ammonia which he uses in his refrigerating system. If anything goes wrong with his plant he is very apt to blame the ammonia, which he is using, for the trouble. These facts must be taken into consideration when an engineer criticizes any given brand of liquid ammonia. It may be that the ammonia is not at fault at all, but that bad management, bad operation or leaks are responsible for the trouble. Nevertheless, there is a certain amount of agreement among engineers all over the country as to the quality of certain brands of liquid ammonia sold for refrigerating purposes. This agreement is so general among engineers at widely isolated points, that it must be given a good deal of consideration in forming an opinion as to the quality of any given brands. Criticism of certain makes of ammonia were so persistent that it became necessary to investigate a number of different brands on the market with the idea of determining, if possible, what brand was best to use and what one worst for refrigerating purposes. The ammonias investigated will be referred to by letters A, B, C, D, and E, and the quality of the different brands was in the order given, A being the best and E the worst.

To determine the residue after evaporation, use was made of the apparatus described by Dr. F. W. Frerichs.<sup>1</sup> From one to five lots of 100 cc. each were evaporated slowly either in the air or in a calcium chloride bath, the

latter being used to avoid the accumulation of snow and ice on the bulb. The evaporation was conducted until the ammonia was boiled off, but no longer than this, when the volume of the ammonia was read off. The results by this method were as follows from 500 cc. of the liquid ammonia: "A," 0.05 cc.; "B," 0.05 cc.; "C," 0.05 cc.; "D," 0.075 cc.; "E," 0.10 cc. These residues all consisted of dark oily-looking matter containing some iron oxide. The residue was darkest in the case of sample "E" and lightest in the case of "A," and the colors were pretty well graduated from "A" to "E." The amount of residue obtained indicates that the ammonia now sold on the market is nearly free from substances non-volatile at the temperature of boiling ammonia; but a most suggestive point in connection with these results is that many engineers at different points from their experience with different makes of ammonia grade them just as they would be graded from the results of these evaporative tests, that is, engineers who have never made or seen any chemical tests in their experience would grade the various makes of ammonia from their experience just as they would be graded by these evaporative tests.

It was thought that some information as to the quality of the ammonia might be obtained by investigation of the non-condensing gases, or rather of the non-basic gases dissolved in the liquid ammonia. Among the non-basic gases would be included practically all of the non-condensing gases likely to be present and also carbon dioxide. For this purpose the drum was supported in the ordinary position for drawing off liquid, Frerich's apparatus was attached for convenience in drawing off and the following apparatus was made use of: a 50-cc. gas measuring burette graduated in 1/10 cc., with stop-cock in the upper end, was sealed by its open end to the bottom of a flask of convenient size, say 1,000 or 2,000 cc. capacity approximately. This apparatus was filled with standard sulphuric acid of convenient strength, say  $N/2$ ,  $N$  or  $2N$ , and inverted in the same acid contained in 1,000 or 2,000 cc. evaporating dish. The total volume of acid used is known; the acid is colored by means of cochineal indicator. A long narrow delivery tube of glass with end bent upwards is connected with Frerich's apparatus by means of a strong piece of rubber tubing. The valves are now opened and a small quantity of ammonia allowed to pass through the delivery tube in order to clean it out. While the ammonia is still issuing from the tube in a slow, steady stream it is suddenly thrust under the gas-collecting apparatus; the ammonia is allowed to pass into the standard acid until this is saturated, which is shown by the change of color of the cochineal indicator. The acid must, of course, be suitably agitated. At the saturation point the tube is quickly withdrawn and the gases afterwards drawn off into a

<sup>1</sup> THIS JOURNAL, 1, 368 (1909).



Hempel gas-measuring burette and measured. The amount of ammonia drawn off is calculated from the amount of acid saturated, which may, of course, be any convenient amount, and the volume of gas obtained in the gas-measuring burette may be calculated to unit weight or volume of ammonia, whichever is desired. The results obtained by this method calculated in cc. of gas per gram of ammonia were as follows: "A," 0.148 and 0.128; "B," 0.124, 0.129 and 0.107; "C," 0.166 and 0.156; "D," 0.163 and 0.139; "E," 0.293, 0.328 and 0.313. These amounts showing the gas dissolved in the ammonia, while not very large, places the various brands of ammonia in approximately the same order that they are placed by operating engineers. Brands "A" and "B" are generally considered above criticism.

Another method for determining the gases dissolved in the liquid ammonia is easily suggested. Instead of allowing the ammonia to pass into the standard acid to its saturation point, the delivery tube is removed before this point is reached. The gas collected is drawn over into a Hempel gas-measuring burette and measured and the standard acid made up to volume in a volumetric flask of sufficient size and an aliquot titrated with a standard alkali. From the data so obtained the weight of ammonia drawn from the drum can be calculated.

Next the non-basic, or, in other words, the non-condensing gases as ordinarily understood, lying above the liquid ammonia in the drum, were investigated. For this determination the same apparatus was used as in the previous determinations, but the drum was turned over and inclined slightly, so that the gas lying above the liquid ammonia might readily be drawn off. Following this the procedure was identical with that given above and the calculation was the same. "A" showed 0.6, 0.3, and 0.6 cc. per gram of ammonia; "B" showed 1.0 and 1.1; "C" showed 4.4, 3.8, 3.3 and 2.4; "D" showed 27.6 and 21.3; "E" showed 307.0 cc. and 330 cc. Thus in the gas lying above the liquid ammonia and calculated in cc. per gram of ammonia there are shown to be enormous differences in the different makes varying all the way from 0.6 of 1 cc. up to 330 cc. These non-condensing gases represent a considerable loss to the buyer at the outset, inasmuch as ammonia is taken out of these drums under vacuum and any non-condensing gas taken into an ammonia system must be blown off sooner or later, and when blown off it will carry with it a certain amount of ammonia. Further, in the operation of the system non-condensing gases are probably the greatest evil, since they reduce the partial pressure of the ammonia gas in the condenser, and thus tend to elevate the pressure and the temperature of the compressor cylinder. Thus the efficiency of the compressor is greatly reduced, and it is possible too that with the higher pressures, the higher

temperatures required to get the same capacity out of a compressor may result in the actual decomposition of ammonia or lubricating oils. In order to get an idea of the direct loss to the buyer of these non-condensing gases, a drum of ammonia was balanced on a small platform scale in an inverted position, so that the gas lying above the liquid ammonia could be drawn off, use was made of Ferich's apparatus connected to a long, narrow delivery tube and the gases were drawn off into tubs of cold water until all of the issuing gases were absorbed by cold water or acid, thus indicating that nothing but basic gases, or practically pure ammonia, was coming off. The drum was then weighed back and the loss figured. This loss, of course, included not only the non-condensing gases but also ammonia itself. However, the same loss of ammonia would result when non-condensing gases are blown off from the ammonia system. Under this test brand "A" showed no loss, that is, the loss was too small to be weighed on the scale used; brand "B" showed a loss of  $1/4$  lb. to the drum; brand "C" showed a loss of  $1\frac{1}{4}$  lbs. per drum; brand "D" showed a loss of  $4\frac{1}{2}$  lbs. per drum; brand "E" showed a loss of 3 lbs. per drum. Here again there is a rather startling difference between different makes of ammonia. The writer does not want to suggest that all the troubles in the refrigerating plant are due to non-condensing gases coming from the drum of ammonia used, but that these gases can and do cause trouble in a system there should be no reasonable doubt. Further, that liquid ammonia can and should be made free from such gases is also beyond question. Analyses of the non-condensing gases from the various drums were made by Hempel's methods and it was found that these gases consist for the most part of air with, however, a lower percentage of oxygen than corresponds to atmospheric air. It is possible, and not unlikely, that some of the oxygen has been used up in the oxidation of lubricating oils or the oxidation of the drum or other metal parts of the manufacturing apparatus. Hydrogen is present only in small quantity, the percentage found being 3 per cent.

A sample of gas taken from the top of the condenser of a well-regulated and well-operated ammonia plant, in which no high pressures or temperatures had been recorded for a good many weeks, showed practically the same composition as the gases from the above liquid ammonia in the drums.

As specifications for anhydrous ammonia, based on the results of this investigation, I should say that the total residue by the method described per 100 cc. of acceptable ammonia ought not to be greater than one-tenth of 1 cc.; the non-condensing gases dissolved in the liquid ammonia ought not to be more than 0.12 of 1 cc. per gram of ammonia; the non-condensing gases lying above the liquid ammonia ought

not to be greater than 0.6 cc. per gram of ammonia; and the whole drum, when tested on a scale by the method described, should not show any appreciable loss.

It is possible that the amounts of impurities here reported might not be regarded as serious by the makers of ammonia; however, this work establishes the fact that anhydrous ammonia is being made and can readily be made of the purity required by the specifications, and there is no reason why any ammonia should be sold which does not come up to these standards. That a good deal of trouble is caused in refrigerating plants by the ammonia used there can be no question, because the universal testimony of reputable engineers is to this effect. That a part of it at least may be due to non-condensing gases in the drum is easily believable.

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## ADDRESSES.

### THE IMPROVEMENT OF ANALYTICAL PROCESSES.<sup>1</sup>

By W. D. RICHARDSON.

Following Bergman's suggestions and the prominent and successful use of the chemical balance by Lavoisier, the art of quantitative chemical analysis developed with fair rapidity, until in the early half of the nineteenth century many chemists were adept in it. Practically all of this development came through individual effort and experience. There was practically no concerted action, little coöperation in the development of methods of analysis. One by one the methods were developed and put upon a working basis. They were systematized and systems of mineral analysis appeared. Qualitative analysis was developed to a high point of perfection, already in the forties of the nineteenth century. A fair system of quantitative mineral analysis was developed and used not many years later. From this beginning quantitative analysis developed more and more along the line of special methods, assay methods, they might be called, where one constituent only was sought for among all that might be present; and the methods tended more and more to attain speed without sacrificing accuracy. In the end analysis became more and more a matter of formula and less and less a matter of carefully thought-out plan on the part of the analyst performing the work. Fresenius foresaw that quantitative analysis might take this turn and repeatedly warned the student to plan his work carefully before commencing operations.

Analysis is the distinctive art of chemistry, and chemists must universally regret a decline of the art, yet we must acknowledge that there has been a decline to a greater or less extent which has accompanied the reduction of analytical processes to recipes and formulae. Because it was possible to teach a boy of no special education or preparation one or more methods of chemical analysis, so that he could perform the operations and obtain good results, the chemist came to look upon analysis as a more or less perfunctory and disagreeable duty which he was called upon from time to time to perform. This was particularly the case and is still the case to a large extent, because of the applications of chemistry to manufacture and engineering, which to many at the present time appear to be nobler and higher callings than that of analytical chemistry.

<sup>1</sup> An address before the Division of Fertilizer Chemists, American Chemical Society, Boston meeting, December, 1909.

With the decline, as I call it, of the art of analysis came the realization on the part of many chemists that steps must be taken to insure accurate results in chemical analysis at all hazards, because it was seen that inaccuracy prevailed far too widely in the work. In the eighties, in this country, the work was taken up systematically, particular credit being due to the American Association of Official Agricultural Chemists, who first investigated the methods of analysis as applied to fertilizers, and formulated methods of analysis which would yield, in average hands, good results. Their efforts were eminently successful, and while we must agree at the outset that no amount of care in formulating methods can take the place of good analysts and accurate manipulation, nevertheless the former are necessary forerunners of good results. The procedure used by the A. O. A. C. and by other organizations in dealing with analytical methods characterize the present time in analytical chemistry. While the invention of new analytical methods by individuals will still continue, nevertheless the working out of these methods, their standardization, is being done now and will be done in the future by committees and the collaboration of many chemists. Since this is the tendency of the present times, it may be well to consider the important features of the work as now performed.

In the first place, the dictum that chemical matters should be handled by chemists will hardly be gainsaid, certainly not by one of the profession. It is only equivalent to saying that legal matters should be handled by lawyers and medical matters by physicians. It happens in the case of the chemical profession that applied chemistry is a large factor in many manufacturing lines and that manufacturers and associations of manufacturers are largely interested in analytical processes. It also happens that the manufacturer dealing with chemists under his control and commercial chemists outside of his line has returned to him every now and then results which lead him to lose faith in chemists and chemical processes. This usually happens when he sends out the same sample to different chemists and has different results returned. Such results lead him into action looking like self-protection in similar cases and to the improvement in some way of existing conditions, so that such things may not recur. He may correspond with one or all of the chemists and ask for explanations. This will probably be his first step. He will probably also avoid as much chemical work as possible in the future and he may request the commercial organization to which he belongs to investigate the matter. That organization, in its investigation, may appoint a committee to consider the methods which chemists are using for certain determinations, and this is the point about which I wish to speak particularly.

It seems as though the appointive powers of committees interested in the investigation of chemical analysis or any chemical matter ought to rest with responsible chemical organizations. As I see it, the manufacturer or chemical association's committee ought to go no further than to lay the whole matter before the proper chemical society and ask for action. It goes without saying that a chemical society to whom such matters are referred should extend friendly and accurate assistance to the adjustment of the difficulty, and to the matter of the criticized processes. As to the association or society of chemists which should take such matters under consideration, I have nothing further to suggest than that they should be truly representative, and by representative I mean that any chemist interested in the particular field concerned should be eligible to membership. This has been the only serious criticism and drawback to the work done by the A. O. A. C. Many chemists interested in a particular line of work, whether fertilizer or food work, are excluded from this association. The answer to this may be that the methods developed by the A. O. A. C. are developed principally for guidance of their own

members and that others need not use them unless they desire to. But from the official positions occupied by the men composing this association, other chemists are practically forced to use the methods whether they desire to or not. These statements are made without any desire to criticize the A. O. A. C. or the splendid work which it has done. This association developed fertilizer and food methods when these were in a chaotic condition, codified them and put them on a sound scientific basis. Too much praise cannot be given to their work. Nevertheless, it is my opinion that when such work is undertaken from now on, it should be undertaken by associations to which all chemists interested should be eligible to membership. These, then, are my first two points, that chemical matters should be handled by chemists, and the association or society handling them should be truly representative. Of course the work should be taken in hand by committees and the work should be done by collaborators. Now a committee, to do its best work, should not be so large that it is cumbersome. All that is needed in working on methods of analysis is a small and active group of men who will undertake the general guidance of collaborators and the calculation of results. For most work, I should say that a committee need not be composed of more than three or five men, in extraordinary cases, of seven or nine men, when it is desired to have sub-committees. Large committees will certainly prove cumbersome, and the same results may practically be attained by the selection of a larger number of collaborators. In the selection of collaborators, only those should be approached who are known to have had wide experience and to have been successful in the particular branch under consideration. For this reason, when the collaborators are once appointed, the work of each must be given equal credibility and each result must be figured into the final average. After the results are in, it is too late to say that the work of this or that collaborator is to be taken at more or less than its face value. In other words, the possibility of poor results should be excluded at the time the collaborators are appointed. As to the number of collaborators, provided they are of high standing, the more the better. In sending out the samples it is a wise plan if they are so sent out and so prepared that they may, after the analytical results are returned, become standard samples and to which reference may be had at any future time in checking up analytical work. I am glad to see that this has been the method adopted by some of the committees of this Division in their recent analytical work on methods of fertilizer analysis. Standard samples should become most important aids in accurate chemical analysis in the future. In some branches, notably in iron and steel analysis, they have already become of great assistance in working out new methods or checking up old ones, also in checking up analysts at the commencement of their work. Let us by all means have more standard samples sent out, and there is no better time for sending them out than at the time collaborative analytical work is undertaken. In this way the average of the best agreeing results of different workers may be taken as the true percentage of the various ingredients contained in the standard sample. Of course, it would be wise to keep in reserve an extra lot of these standard samples to be sent out from time to time on request for a nominal cost. Happily the Bureau of Standards has undertaken this work for some lines of analysis, and I desire to express the hope that they will extend their good work to other lines as rapidly as circumstances will permit. In such work the Bureau should have the hearty support of all chemists and chemical organizations.

I believe it would be well for this Division to appoint a committee to correspond with the Bureau in the endeavor to have standard fertilizer samples prepared and kept on file at the Bureau for distribution. In the meantime, our own committees have been preparing and sending out samples for coopera-

tive analytical work, and these samples, if carefully preserved by the collaborators, will serve as standards after the best results have been averaged. It should be mentioned that standard fertilizer samples containing much bone should have a low moisture content or they should be preserved by means of an antiseptic, otherwise the moisture content—the determination of which is receiving increased and well-deserved attention—will be greatly altered by the growth of fungus.

When sending out samples for collaborative work, one of two methods may be adopted. Either precise instructions concerning the method of analysis to be employed should accompany the sample, or the sample may be sent out with the request that the method commonly used by the recipient be employed. In the latter case, the work would naturally be preliminary to the development of a final method and a number of well-directed questions concerning the method employed may well accompany the sample. Such definite questions will insure intelligent and general answers as to the method employed. It usually happens that various laboratories use modifications of standard methods, very slight in themselves, but which may in the long run affect results more or less. In compiling results, such data should be in the hands of the steering committee. When the details of any method which does not yield good results are finally put together, the result of course resembles more or less a cook book recipe, and every chemist must regret the necessity of reducing analytical processes to such an empirical basis. It is certainly the desire of every one to obtain by his analytical work not only agreeing results but results which express accurately the absolute amount of the ingredient sought which is present in the sample. The reply must be made to such a criticism, if this be permitted, that such methods have become a commercial if not a scientific necessity, and in my opinion they have become as much a scientific necessity as a commercial necessity. Experience has shown that unless our methods of analysis are reduced to exact formulae, results obtained will in many cases be pitifully absurd and worse than useless. It is painful to recall certain instances of samples sent out for chemical analysis by some chemists in the past, but the instance of the zinc ore and the clay limestone sent out not so long ago by the Committee on Uniformity in Technical Analysis will serve as sorrowful and classical examples.

In conclusion, I wish to express the hope that in the development of future analytical processes, the various divisions of the American Chemical Society will in this country take a prominent part and that their work along this line may be guided by the good judgment and careful consideration which has characterized the first work undertaken by the Division of Fertilizer Chemists.

## CONSERVATION AND UTILIZATION IN THE PACIFIC NORTHWEST.<sup>1</sup>

By H. K. BENSON.<sup>2</sup>

Received February 17, 1910.

The problem of conservation in the Pacific Northwest is vitally related to that of utilization. While the former is largely an attitude of mind, the latter is a duty of the hour and upon it depends the development of Western Washington.

We have in the Pacific Northwest no great chemical industries that may be regarded as prodigate in their wastefulness. The sources of waste where the processes of utilization might be called into service are few in number. One of these is the waste of fruits and vegetables amounting annually to hundreds of tons which might be converted into ethyl alcohol by a sys-

<sup>1</sup> Read before the Puget Sound Section of the American Chemical Society, February 5, 1910.

<sup>2</sup> Associate Professor of Industrial Chemistry in the University of Washington.



tem of municipal utilization. The economy of the process of utilization has been the deterring factor in this case.

The most apparent instance of waste is the lumber industry. Here each mill has in use large burners for the consumption of waste wood. Much of this is rich in resinous matter and might profitably be subjected to steam distillation for the recovery of a volatile oil which yields a high percentage of turpentine and about 10 per cent. of fir oil together with some resin. The wood, after being thus distilled, might be used for producer-gas manufacture or used for wood products of various kinds. The cause of non-utilization in this instance is apparently the technical and somewhat experimental character of the process of utilization. The lumber industry is overwhelmed with the yield of its product and regards its waste merely as matter for speedy disposal.

The greatest example of waste is another by-product of the lumber industry—the logged-off land of the Pacific Northwest—the stubble of the lumber harvest. From more than two and a half million acres of land on the western slope of the Cascade mountains, in Washington, the timber has been removed and a tangled mass of débris and charred and blackened stumps have been left as the heritage of the forest to the farm.

It is nevertheless upon the existence of the latter that the development and prosperity of the Pacific Northwest is dependent. It has been found, upon careful analysis, that less than 10 per cent. of the foodstuffs consumed are produced locally. The demand for the products of the farm is met almost entirely by shipments from the older agricultural communities. To avoid the cost of the long haul, the logged-off lands must be utilized for supplying the needs of our cities and commercial centers.

An effort to bring about the utilization of these lands for agriculture and fruit-growing is being made by coöperative work between state institutions and the federal government.

The first obstacle in the way of utilization is the cost of land-clearing. This ranges from \$25 to \$250 per acre. When at its cheapest, it requires the use of high-power machines and skilled labor.

The Bureau of Plant Industry of the U. S. Department of Agriculture, working in cooperation with the State Agricultural Experiment Station and the Department of Chemistry of the State University, seeks to both cheapen and simplify the process. This is to be done by a number of lines of work.

1. *Standardization of Cost of Land-Clearing by Present Methods.*—By making a careful study of the size of stumps, their method of rooting, condition, amount of powder used and labor employed, a correct estimate of the cost may be obtained.

2. *Simplification of Process of Land-Clearing.*—The object here is to replace the donkey engine and its crew by the farmer and his team. A number of methods are being tried out on an experimental scale in the field. The simplest is that of char-pitting where the process of charcoal burning is applied to the stump. A quantity of kindling wood is piled about the stump, covered with soil and fired from the windward side. The principle here is the conservation of heat to char and disintegrate the stump. The next step is to use air-tight metallic hoods with long stacks, the method of operation being similar to that of down-shaft furnaces.

3. *Cheapening the Cost of Land-Clearing by the Sale of By-products.*—The removal of stumps may be brought about by the use of modern stump pullers operated by a team of horses. The stump thus removed may be subjected to destructive distillation. The products thus obtained are pyroigneous acid, wood tar and charcoal. A local market exists for the latter but it is necessary to find suitable markets for the former, and the trade is now being solicited for the form in which these products should be prepared for the market.<sup>1</sup>

<sup>1</sup> The writer will be pleased to hear from the manufacturing and

A second obstacle in the utilization of the logged-off lands of Western Washington is the lack of definite methods of agriculture for certain types of soils. To pass upon the conditions of agriculture, the Bureau of Soils of the Department of Agriculture and the State Geological Survey made a field examination of a portion of the logged-off lands. They classified the logged-off land in five classes: (1) Land suitable for extensive agriculture; (2) Land suitable for pasture, fruit-growing and intensive farming; (3) Land that can be utilized for intensive farming but better adapted to orchards; (4) Land suitable for reforestation only; and (5) mixed class or small areas of agricultural land scattered over large areas of non-agricultural land.

The limited agriculture of Western Washington has followed the alluvial deposits of water courses and the lowlands formed from old lake beds and rained marshes. In utilizing the upland soils, the glacial origin of the soil must be considered. If we trace the history of the prolific forest which has been removed from the glacial soils, we can better understand the nature of the problem that confronts us in the development of Western Washington.

First those great tablelands of coarse, rugged rock débris, the weathering agency of centuries on the surface, the porous, sieve-like structure underneath, the gradual accumulation of vegetative growth and its decay—these are the primary elements of the upland soil formation. Then come the efforts of nature to conserve the moisture above the sieve by causing the adaptation of plants to the trailing and bending type, thus giving the largest covering surface, and favoring the exclusion of evaporating agencies. In these hidden recesses the seed of the tree at last is borne, and germinates, and, fed from the hiding place of the raindrop, grows into its full stature and nature into the mighty forests of the Northwest.

Now comes the lumberman and cuts down the forest, then the fire burns off every living blade, and, thus, in the course of a few years, the work of centuries is undone and the jungle of magnificent forest is become the desert of ruin and desolation.

Yet the soils of the uplands are above the average in the elements of plant food. Hilgard<sup>1</sup> gives as the average of 696 samples of soils taken from the humid region the following percentages of the main elements of fertility: Lime, 0.13; phosphoric acid, 0.12; potash, 0.21; and the loss on ignition, 4.40. The average analysis of 71 samples of the upland soils of Western Washington gives the following results: Lime, 0.21; phosphoric acid, 0.12; potash, 0.21; and loss on ignition, 10.14. The analysis<sup>2</sup> of cultivated soils in this same region gives a higher yield of lime, showing that the unlocking of lime from the glacial rock particles is brought about by cultivation along with the usual weathering agencies.

The constant cultivation by extensive farming and the adaptation of crops to conserve moisture seem to be fundamental conditions in the utilization of the upland soils.

Where these methods fail on account of the porous, sieve-like structure underneath, there it is necessary to again have the forest gain its foothold, thus bringing about the conservation of forest resources for future generations through the rational utilization of the same resources by the present generation.

Related, as it is, to the immediate life of this community, the utilization of two million acres of waste and encumbered land is truly the greatest problem this part of the Pacific Northwest faces. Its solution is dependent upon the services of science and technical skill in coöperation with the intelligence and good judgment of the people who will occupy these lands.

UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

industrial chemists relative to the uses of pyroigneous acid and tar from fir stumps.

<sup>1</sup> Soils, E. W. Hilgard, p. 377.

<sup>2</sup> Bulletins Nos. 13, 55 and 85, Washington Agricultural Experiment Station.

ADDRESS DELIVERED BY DR. L. H. BAEKELAND AT THE  
CHEMISTS' CLUB IN NEW YORK, ON THE OCCASION  
OF THE AWARD OF THE PERKIN MEDAL  
TO DR. EDWARD GOODRICH ACHE-  
SON, JANUARY 21, 1910.

*Mr. Chairman, Ladies and Gentlemen:*

I ought to start with an apology for myself as well as for the Perkin Medal Committee: if the committee did not select a better man than me to express more eloquently the merits of to-night's laureate, this is solely due to the fact that I happen to be, just now, the president of the American Electrochemical Society. Dr. Acheson is the Past President of our Society, and one of its founders, and has always been one of its most devoted and distinguished members. Furthermore, his main work has been along lines where the electric current is used to accomplish chemical reactions.

What is more to the credit of Dr. Acheson than anything else is the fact that he undertook experiments which probably had been attempted several times before without success by people who had more theoretical preparation than he. But his unusual keenness of observation, his common sense logic, and more than anything, his appreciation of what was of preponderant importance, and of secondary interest, brought him results where others had failed and by which he opened a new field of chemical investigation and industrial applications.

Dr. Acheson stands as a living example to many a chemist, loaded with theoretical knowledge and paper wisdom, and light in judgment or common sense. He entered into a new road with very little knowledge to go by, but he had an open mind, a fertile brain, a constructive purpose, and all the talents of the tireless, intelligent experimenter; his theoretical knowledge he made himself, or picked it up by and by along the road he was pursuing, while he himself was building that road. Whatever he took up, he started from the very beginning and developed it to the very end.

His very insuccesses he turned into practical channels, to change them into victories. He started his work on carborundum by an experiment so simple and so meager in results, that few people, if any, would, like himself, have found in this a spur to further investigation. Later on, when in the manufacture of carborundum, he had to battle with irregularities due to a partial dissociation of the silicon carbide, which thus spoiled his product, he tried by a more powerful action of heat to carry this dissociation to the extreme limit; he so created a new industry, the manufacture of artificial graphite. In the same way he turned irregularities, due to oxidation or partial reduction, into a new field of study and research and gave us siloxicon, a product which seems to have a considerable future in store.

I shall not attempt to describe here the history of the work of Dr. Acheson. He, himself, in a memorable address, delivered in Boston before the American Academy of Arts and Sciences, when the Rumford medal was awarded to him, has given us a most fascinating account of this subject, and to those of my fellow chemists who have not read his "Seventeen Years of Experimental Research," I can recommend it as an inspiration.

Never did the University of Pittsburg award an "honoris causa" degree to a more worthy man than when the doctor's degree was conferred upon our distinguished friend.

In the making of the great road of industrial progress, very few of us are pathfinders; some are surveyors, other ones constructors, others again are merely switchmen, brakemen, and conductors. Dr. Acheson not only was a pathfinder, but he has been constructor, conductor, switchman—everything. By his manifold abilities and good judgment he has been able to develop his discoveries to the point where they became a commercial success. He has shown us that an inventor or a

scientist does not have necessarily to be a theoretical dreamer unfit for executive or practical work.

Dr. Acheson has another great claim of recognition upon us; successful as he has been in his enterprises built on the result of his inventive genius, he has never ceased to make us feel that he was near to every one of us. He always took an active part in the work of our chemical societies, where his presence and his papers have stimulated many of us, younger in experience, or less successful in our efforts. In many instances he has allowed our chemical societies to inspect the plants where his industrial processes are carried out, and he has never hesitated to publish the results of his research work. He has thus set a praiseworthy example to such of our manufacturers, who try to insure by uncompromising secrecy and seclusion the money-making end of their enterprise.

Dr. Acheson, in the name of the American Electrochemical Society, I congratulate you on this recognition of your splendid work, and I congratulate the Perkin Medal Committee just as much in their choice of you.

## NOTES AND CORRESPONDENCE.

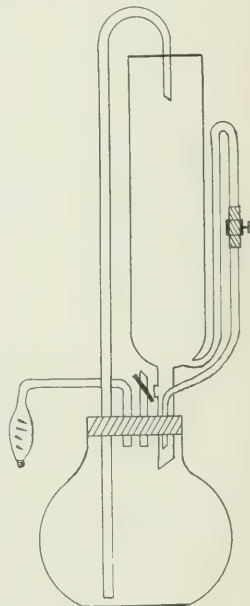
### PERCOLATION.

For percolation of substances which are difficult, if not impossible, to percolate in the usual manner, I have used a Soxhlet extractor, arranged as below, with excellent results:

The extractor is supported by a clamp; a thin layer of glass-wool is loosely packed at the bottom, making sure that the outlet is completely covered. The substance to undergo percolation is then introduced and allowed to remain as loosely as possible; on top of this another layer of glass-wool is placed to hold the substance in place. A beaker is then placed under the extractor, to receive the extract, and the solvent is allowed to drop from a reservoir, the drop being regulated by a screw-clamp. The extract in the beaker is transferred to the reservoir and again allowed to pass through the substance, till the desired strength extract is obtained.

FRANK M. DAVIS.

MACANDREWS AND FORBES CO.,  
CAMDEN, N. J.



### NOTE ON THE RECOVERY OF WASTE PLATINUM.

For some time it has been our custom to collect the alcoholic wash obtained in potash determinations, before the ammonium chloride is run in. This is put in tightly-stoppered bottles and placed on a table in the direct sunlight. After a few weeks it begins to lose its color, and a coating of platinum black is seen on the bottom and sides of the bottle. This action goes on until the solution is entirely clear, and all the platinum has been deposited. The solution may then be poured off and the platinum collected and purified. The platinum is likewise

thrown out and may be collected if the alcoholic solution is distilled off. With equal ease the platinum may be recovered from the potassium platinochloride obtained when the crystals are dissolved from the Gooch crucibles.

If a little alcohol is added to this solution and it is allowed to stand in direct sunlight for a few weeks, the bottles being kept tightly stoppered, the platinum is finally deposited as platinum black and a clear solution remains. The platinum may then be collected and purified as in the case of the alcoholic wash.

A. W. BLAIR.

FLORIDA AGRICULTURAL EXPERIMENT STATION

### THE TRUE MELTING POINT OF TRINITROTOLUENE.

Inasmuch as the determination of the purity of the C. P. trinitrotoluene of commerce is based to a large extent on the melting point, an accurate determination of the true value of that constant has become of importance. The trinitrotoluene in question is the  $\alpha$ -2-4-6-compound, and is obtained as the final product by nitration of C. P. toluene with a mixture of nitric and sulphuric acids.

The crude product is purified by recrystallization from suitable solvents, alcohol being the one usually used, and it is then obtained in the form of small prismatic crystals of a light yellow or brownish color.

The true melting point of the C. P. material has been generally accepted as  $82^{\circ}\text{C}.$ , according to Beilstein, Richter, etc. The authority for this melting point is Wilbrand,<sup>1</sup> who described the preparation of the substance in 1863, and stated that the melting point is "etwa  $82^{\circ}$ ." Later, in 1875, E. J. Mills<sup>2</sup> prepared trinitrotoluene in two ways: His first product from nitrating toluene with fuming nitric acid and then treating with a mixture of fuming nitric and sulphuric acids, with recrystallization from naphtha and alcohol, had a constant melting point of  $78.85^{\circ}$ , which was not changed by boiling 36 hours with fuming nitric acid.

A second product was obtained by treating "solid," by which presumably para mono-nitrotoluene is meant, with fuming nitric and sulphuric acids. This product, when purified, had a constant melting point of  $80.54^{\circ}$ .

In a later article Mills,<sup>3</sup> in 1882, determined the melting points of various benzene derivatives, which were most carefully purified by recrystallization, and found  $78.85^{\circ}$  for the melting point of trinitrotoluene.

The subject has been investigated at the Eastern laboratory, and all available samples of trinitrotoluene that were supposed to be pure were tested with the following results:

	Melting point.
1. Sample of 1-2-4-6 trinitrotoluene from Kahlbaum .....	$80^{\circ}$
2. Another sample of 1-2-4-6-trinitrotoluene from Kahlbaum .....	$79.8^{\circ}$
3. Same sample crystallized three times from alcohol .....	$80.1^{\circ}$
4. Crude English trinitrotoluene recrystallized three times from alcohol .....	$80.6^{\circ}$
5. Samples from various lots of English C. P. trinitrotoluene .....	$80.5^{\circ}$ - $80.6^{\circ}$
6. Trinitrotoluene manufactured at the Eastern laboratory from commercial C. P. toluene and recrystallized .....	$80.5^{\circ}$

Finally, in order to determine the true melting point of trinitrotoluene, commercial C. P. toluene was carefully fractionated in the laboratory until a large quantity of a product boiling constant at  $110.7^{\circ}$  (corrected) at 760 mm. pressure was obtained. This was nitrated in the usual way with a mixture of nitric and sulphuric acids, and the product recrystallized.

A product with a sharp melting point at  $80.6^{\circ}$  (corrected) was obtained.

This product was further nitrated again with a mixed acid of the same composition, but the melting point of the product was not changed thereby.

The melting point determinations were made most carefully by the capillary method, using a fine capillary and the smallest possible amount of substance. The melting points in all cases were sharp, and the necessary corrections for emergent thread were made.

The experimental work connected with this investigation was carried on by Dr. C. M. Stine and Mr. C. C. Ahlum, to whom I wish to express my thanks.

A. M. COMEY.

EASTERN LABORATORY.

E. I. DUPONT DE NEMOURS POWDER CO.,  
December 22, 1909

### NOTE ON A CONDENSER USED FOR EXTRACTION.

Its main advantages are (1) that it has a large cooling surface (necessary in the case of low-boiling solvents) and (2) that the solvent may be almost wholly recovered while the flask is still connected to the condenser (economical in the case of extractions by ether, acetone, etc.).

The total length of the condenser is thirty-five (35) inches. It has been used together with flasks similar to those described by Albert P. Sy,<sup>1</sup> for about a year and has given satisfaction. Instead of a platinum perforated disk extraction tube, one having a diameter of thirteen-sixteenths ( $13/16$ ) inches at "A" (see figure) and seventeen-sixteenths ( $17/16$ ) inches at "B" is conveniently used. The substance to be extracted is weighed into a ( $22 \times 80$  mm.) thimble, which easily fits into the tube.

DAVID BLOOM.

### BUREAU OF STANDARDS, ANALYZED SAMPLES.

The Bureau of Standards, Washington, D. C., is ready to distribute Bessemer steels with 0.6 and 0.8 carbon, and an iron C to replace that originally prepared by the American Foundrymen's Association. The new C has the following composition: Total C, 2.78; graphite, 2.22; Si, 1.84; Ti, 0.074; P, 0.192; S by oxide, 0.0354; S by evol., 0.0335; Mn, 0.744.

A new iron B was found to need remixing and partial analysis. It is hoped that the sample will be ready to distribute by the time this notice appears in print.

A vanadium steel and an ore of manganese await the reconciling of differences in the analytical results reported.

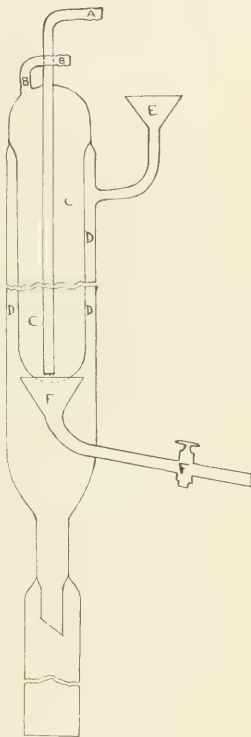
Three Lake Superior iron ores are undergoing analysis: one to serve as a standard for iron, phosphorus and silicon; the

<sup>1</sup> THIS JOURNAL, 1, 314 (1909).

<sup>1</sup> *Annalen*, 128, 178.

<sup>2</sup> *Phil. Mag.*, [4] 50, 17.

<sup>3</sup> *Ibid.*, [5] 14, 27.





second for aluminum, calcium and magnesium; and the third for manganese.

#### POSSIBLE CONTAMINATION OF ACETIC ANHYDRIDE USED IN THE LIEBERMANN-STORCH REACTION.

The note by Waters and Bencker on casein tests,<sup>1</sup> with incidental reference to the Liebermann-Storch reaction for rosin, calls attention to the fact, not sufficiently emphasized in the books, that this test gives positive results with many gums, waxes, and oils. Further, much of our acetic anhydride comes with the glass stopper sealed with a wax which itself gives the Liebermann-Storch reaction. This should be noted, for unless the stoppers are cleaned, carefully and scrupulously, the acetic anhydride may be itself so charged with resinous material as to appear to give the test, even with substances which are really neutral or indifferent to the test. That the acetic anhydride bottles so sealed are from a leading drug-and-chemical house is only another illustration of the necessity for eternal vigilance in watching the purity of our reagents.

CHAS. S. PALMER.

NORWOOD, MASS.

#### BOOK REVIEWS AND NOTICES.

**A Text-Book of Botany and Pharmacognosy.** By HENRY KRAEMER, Ph.D., Professor of Botany and Pharmacognosy of Philadelphia College of Pharmacy. Third revised edition. 850 pp. Philadelphia: J. B. Lippincott Co.

The subjects are classified as follows: Part I, Botany. Part II, Pharmacognosy: Chapter I, Crude Drugs; Chapter II, Powdered Drugs and Foods. Part III, Reagents and Microscopical Technique. The sections devoted to botany are abundantly, accurately and excellently illustrated, while the subject-matter is presented in an unusually clear manner. Under Pharmacognosy of the Crude Drugs, we find the information relative to their chemistry, thorough and up-to-date. The common adulterants and also the allied plant products are detailed under each drug, a knowledge of which is of primary importance to-day, when adulteration and substitution among crude and powdered drugs is so prevalent. The chapter on Powdered Vegetable Drugs and Foods is especially recommended to food and pharmaceutical chemists, a subject so little known and of such primary importance since the enactment of the Food and Drugs Act. Any analyst upon carefully studying this chapter will discover the invaluable uses of the microscope, an instrument very much neglected in our chemical institutes. The chapter devoted to reagents and methods of staining, mounting and micrometry is a valuable feature, but still more to be commended is the application of the micro-polariscope, so very useful in this as well as other branches of chemical research. Professor Kraemer is to be congratulated in having presented an original and valuable reference as well as text-book, which should occupy a prominent place on the shelves of every food analyst.

V. CORLENTZ.

**The Manufacture of Paper.** By R. W. SINDALL, F.C.S., London. New York: D. Van Nostrand Co. 1908. Price, \$2.00 net.

This purports to be an elementary text-book which confines itself to an outline of the various stages of the paper manufacture and some of the more recent improvements in the industry. From whatever point of view it is considered, the book must be adjudged a contribution of very moderate value to the literature of the art. Its material has been brought together many times before and in its present arrangement takes on no new aspect. As a text-book, "The Manufacture of Paper" fails to meet several fundamental requirements. There

<sup>1</sup> THIS JOURNAL, 2, 28 (1910).

is no clear statement or logical development of general principles, definitions are often inexact and descriptions superficial rather than concise. Cellulose, for example, is hardly to be defined as "paper pulp" or even as "this fibrous substance." We do not speak of "a vegetable plant." Parchment is quite a different thing from parchment paper. Celluloid is not always "a plastic, ivory-like substance." No reference is made to the necessity of tension if mercerization of cotton is to produce silky luster; the paragraph on artificial silk is carelessly inaccurate and there is no mention under "Viscose" of the regeneration of cellulose through decomposition of the material, although the commercial developments of viscose are based upon this regeneration. There are 58 illustrations, most of which can be of little assistance to the student through lack of adequate description in the text. The chapter on the chemicals used in paper making is most casual in its treatment. The best parts of the book are those which relate to beating, a subject which has been much more fully treated by Beadle, and to dyeing and coloring, which have been far more adequately presented by Eriurt. The book concludes with a valuable bibliography, the most complete which we have seen, and a brief index. A really comprehensive and up-to-date text-book of paper-making is much needed and it should easily lie within Mr. Sindall's powers to produce it. It is to be regretted that he has not done so in the present volume. A. D. LITTLE.

**Allen's Commercial Organic Analysis.** 4th Edition. Vol. I. Edited by HENRY LEFFMANN and W. A. DAVIS, assisted by the following contributors: E. F. ARMSTRONG, J. L. BAKER, G. C. JONES, E. SCHLICHTING and R. W. SINDALL. Philadelphia: P. Blakiston's Son & Co. Large 8vo. Cloth. 576 pp. Price, \$5.00 net.

In preparing the present edition of this well-known standard work, the editors and contributors have followed in the main the arrangement of the previous editions. It has been found necessary, however, to turn over the writing of the various parts to specialists, and in their selection both sides of the Atlantic have been drawn upon, thus making the work international in character. The introduction of the present volume is by W. A. Davis and covers the general methods of commercial organic analysis. Alcohols are treated by G. C. Jones; Malt and Malt Liquors, by Julius L. Baker; Wines and Potable Spirits, by G. C. Jones; Yeast, by Emil Schlichting; Neutral Alcoholic Derivatives, by Henry Leffmann; Sugars, by E. Frankland Armstrong; Starch and Its Isomers, by E. Frankland Armstrong; Paper and Paper-Making Materials, by R. W. Sindall; Acid Derivatives of Alcohols, by Henry Leffmann.

It will be seen from these several divisions that a considerable part of the subject-matter is altogether new, notably the chapters on yeast and on paper and paper-making materials. The number of pages have been increased from 557 to 576, but the increase of matter is more than would be covered by the increase in the number of pages. The descriptive treatment, which characterized Allen's works in previous editions, is retained in the present and is to be commended in a work of this character. Analysts who have used the previous editions with profit will find the present edition valuable, although since it is written by a number of authors, all parts cannot be absolutely equal in merit, and only repeated use will determine the actual merit of the various parts. The paper, typography and binding are excellent.

W. D. RICHARDSON.

**Producer Gas Fired Furnaces.** By OSKAR NAGEL. Large 8vo., cloth, 184 pages. New York: Published by the author. Price, \$2.00 net.

All of Mr. Nagel's works have the merit of covering subjects not otherwise specifically treated in the English language. The work under consideration is made up of some ten chapters and an appendix, in which are to be found descriptions of all

the important types of producer gas-fired furnaces as used in the chemical, metal, iron and steel, lime and cement, glass and brick and ceramic industries, besides chapters on the generation of producer gas, construction of gas producers and combustion of producer gas. The book is splendidly illustrated with 237 cuts and will be found of great interest by all students in this important field, as well as by practical men who make use of producer gas-fired furnaces or who desire to.

**Chemisch-technische Untersuchungsmethoden.** By DR. GEO. LUNGE and DR. ERNST BERL, with the collaboration of E. ADAM, P. AULICH, F. BARNSTEIN, O. BOTTCHE, A. BUJARD, C. COUNCLER, K. DIETERICH, K. DUMMLER, A. EBERTZ, C. V. ECKENBRECHER, A. EIBNER, F. FISCHER, F. FRANK, N. FREUDENBERG, E. GILDEMEISTER, R. GNEHM, O. GUTTMANN, E. HASELHOFF, W. HERZBERG, D. HOLDE, W. KLAPPROTH, H. KOHLER, PH. KREILING, K. B. LEHMANN, J. LEWKOWITSCH, C. J. LINTNER, E. O. V. LIPPEMANN, E. MARCKWALD, J. MEFFNER, J. PAFFLER, O. PFEIFFER, O. PUFAHL, O. SCHLUTIG, K. SCHOCH, G. SCHULE, L. TIETJENS, K. WINDISCH and L. W. WINKLER. Vol I, 6th edition, entirely rewritten and enlarged. Large 8vo. pp. 674 + 72. Berlin: Julius Springer. 1910. Price, paper, 18 marks; bound, 20.50 marks.

It is proposed in this, the sixth edition of Lunge's great work on Technical Methods of Analysis, to so arrange the matter that it will be published in four or more volumes, whereas the fifth edition, which was edited by Dr. Frederick Böckmann, was published in three volumes. The present volume embraces only that part of the previous first volume up to and including potash salts and potash, with an additional chapter on liquefied and compressed gases. It will thus be seen that more than one hundred pages have been added to this edition of the previous first volume alone. It goes without saying that under the direction of its distinguished editors, the present volume will compare in every way with previous editions of this work and will be brought thoroughly down to date.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

On the evening of February 3, 1910, an informal gathering took place at which there were present, among others, most of those to whom had been delegated the task of providing for the creation of an Organization for the Eighth International Congress of Applied Chemistry, by the London Congress last June; a representative of the Association of Manufacturing Chemists, the American Chemical Society, the American Electrochemical Society and the Society of Chemical Industry were each also present at this informal meeting.

The consensus of opinion was that the greatest success could be expected only if the most effective system and mode of organization could be had, and if each and every chemist in the United States could be made to feel that he himself directly or indirectly, through his professional, business or educational affiliations, had a personal share of responsibility in the conduct and management of the Congress from its very start and to its very end. This was regarded as the proper and correct guide in proposing any plans or schemes of organization.

The Eighth Congress is to convene in 1912, with Professor Edward W. Morley as Honorary President and Dr. W. H. Nichols as Acting President, at a time and place to be determined by the Organization of this Congress. The most important of the Congress, in fact that by which its value and real success will be measured, is the amount of original matter, both scientific and technical, which it will be able to present to its members. To this end, every chemist in America who

has or may have any original matter to present to this Congress should begin without delay to prepare such matter, and have it in shape so that it may be presented to the Congress in ample time for proper printing, classification and distribution to members and the technical and scientific press.

The Congress, being held in the United States, will with a great deal of right, and naturally, look to a very good showing from the chemists of the United States, and every chemist in this country, which is to be host to our foreign colleagues, should constitute himself a committee of one to get from himself, or from his friends, as much scientifically or technically valuable material as possible, so that the Proceedings and Publications of the Eighth Congress may correctly reflect the true mental attitude of the chemists of the United States towards their profession, both as a pure science and as a part of the industrial activities of this country.

It is the hope that the Program Committee will be able to begin its activities effectively before the close of 1910, but in the meantime it behooves every chemist in the United States actively and energetically to consider how and in what way he can best contribute to the success of this Congress, and particularly in the direction of papers and communications to the Congress embodying the advance in this field since June, 1909, the date of the last Congress.

At a meeting to be held in April or May, 1910, by those charged with the duty of providing suitable organization for the Eighth Congress, some definite action as to such organization may be looked for. Those who have that responsibility are making every effort to get as many suggestions as to divisions of organization, mode of organizing, and membership of the organization as possible. Every one interested in having this organization on as broad foundations as possible is earnestly invited to present any suggestions that may be helpful in that direction, in writing, by the middle of April, 1910, so that all these suggestions may be properly classified and collated and put in condition for most thorough consideration before the meeting above referred to actually takes place. Such communications may be addressed to the temporary secretary, Dr. B. C. Hesse, 90 William Street, New York City.

### AMERICAN EXPOSITION, BERLIN, 1910.

The committee in charge of the American Exposition, Berlin, 1910, has taken note of the vast importance the chemical and allied industries bear to the trade relations between Germany, Commercial Europe and the United States, and has set aside for the use of the leaders of these industries a few thousand square feet of space for their exhibits.

They have asked such well-known men as H. E. Johnson, a prominent printing ink manufacturer of Philadelphia, R. H. Lersner, of the firm of C. M. Childs & Company, of New York, I. F. Stone, president of the Chemists' Club, also president of the National Aniline Chemical Company, and Eugene A. Widmann, secretary of the H. A. Metz Company, New York, to serve as a committee on the chemical exhibits.

These men, realizing the high compliment paid them and the chemical and allied industries as a whole, have accepted this invitation. Mr. Widmann, chairman of this committee, can be reached at 30 Church Street, N. Y. City.

There is no need of drawing attention to the immense exchange of chemical and allied products between the United States, Germany, and European, as well as Asiatic, countries. One need only glance over the statistics to bear out this statement. Berlin, being the commercial center of Continental Europe, offers a very fertile field for not only the manufacturer of the general line of chemicals, but for the maker of specialties. Buyers from Russia, Norway, Sweden, Poland, Italy, Turkey and other countries, and even Asiatic countries as

China and Persia, gather in this city to obtain the larger percentage of their wants. We Americans should be far-sighted enough to grasp this opportunity to enter a world market, and a chance is given us to exhibit the products of our factories at the coming American Exposition in Berlin, which opens in July and extends to October.

A manufacturer of chemicals and allied products must find a new outlet for the same when an overproduction should occur, and no one can tell when this is liable to happen. By making his wares known in Berlin, his name and brand reach these numerous other countries.

This exposition offers a splendid opportunity to the American manufacturer to compete with his foreign brethren on an equal footing. Should the time ever come when he has accumulated a large stock of his products, which, unless he has a foreign outlet, he must sacrifice in the domestic trade, he will not need to find a new channel as he has already established one through his exhibit in this coming exposition. This opportunity for advertising and getting results should not be passed over lightly.

This Exposition has the endorsement of both the American and German Governments, and has such well-known men as J. Pierpont Morgan as Honorary President, David R. Francis, who was president of the Louisiana Purchase Exposition held at St. Louis, as First Honorary Vice-President, John Wanamaker as Second Honorary Vice-President, Dr. George F. Kunz as President of the Advisory Committee, and Herman A. Metz, former Comptroller of New York City, as Chairman of the Executive Committee for sponsors, while in Germany Prince Henry, of Prussia, is to act as President of the Reception Committee.

When such men as these take an interest in a project of this kind, and set aside a special section for the chemical and allied products of America, it is for the leaders of these industries to reciprocate and show their appreciation by exhibiting their line of goods. We wish one and all of them to take this message to heart and act accordingly.

SECTION CHEMICAL EXHIBITS,  
EUGENE A. WIDMANN,  
*Director.*

## SECOND INTERNATIONAL CONGRESS OF ALIMENTARY HYGIENE AND OF THE RATIONAL FEEDING OF MAN.

UNDER THE PATRONAGE OF THE BELGIAN GOVERNMENT, OCTOBER 4-8, 1910

DEAR SIR:

The authorities of the above Congress have requested me to organize the American Committee and to secure a discussion of the subjects which have been proposed for consideration in the Congress. The business of the Congress will be considered in seven sections, as follows:

### SECTION I.

BIOLOGICAL PHYSICS AND ENERGIES.

*Questions Proposed:*

1. The energy problem in muscular work or intellectual work.
2. The energy needs of the organism at different ages. Nutritive coefficients.
3. Isodynamy in nutritive substances. Discussion of the coefficients of Rubner and Chauveau.
4. The energy value of different foods and of alcohol considered from the calorimetric point of view and from the point of view of physiological utilization.
5. The influence of cooking of different kinds of food and the use of certain stimulants or excitants (coffee, tea, wine, condiments, etc.) on the digestive functions and the energy results obtained therefrom.
6. Methods of calorimetric measurements for man.

### SECTION II.

PHYSIOLOGY AND PHYSIOLOGICAL CHEMISTRY—RATIONAL NUTRITION—REGIMEN AND DIETARY.

*Questions Proposed:*

1. Influence of micro-organisms in the digestion and absorption of food.
2. Influence of the zymases of certain foods, especially milk.
3. The influence of different kinds of drinks taken during meals on the digestive processes.
4. The study of antiseptics and saccharine in food and their influence on the organism.
5. The noxious effects of different kinds of alcohols, ethers, aldehydes and such essences as are found in brandy and other spirits in general.
6. Vegetable diet:
  - a. For muscular work.
  - b. For intellectual work.
  - c. In case of illness or disease.
7. The white man's diet in tropical and subtropical countries.
8. Tables of food composition and values with reference to:
  - a. The energy spent during the process of digestion.
  - b. The average prices of preparing and cooking.

### SECTION III.

HYGIENE OF NUTRITION BACTERIOLOGY PARASITOLOGY AND ALIMENTARY INTOXICATION.

*Questions Proposed:*

1. Means for obtaining healthy milk, especially exempt from tuberculosis germs.
2. The action of dead tuberculosis microbes on the human organism and of toxins destroyed by heat.
3. Methods for the bacteriological analysis of water.
4. Usual and principal water bacteria.
5. Methods of research for the presence of coli-bacilli and typhoid bacilli.
6. Interpretation of results.
7. Required regulations regarding the bacteriological condition of the water of oyster beds.
8. Results of recent etiological research in cases of gastrointestinal origin.
9. Physical or mechanical processes recommended for the preservation of food.
10. Processes of sterilization of foods.
11. Contamination of food on sale in streets, shops, bazaars, etc., and remedies therefor.

### SECTION IV.

COMPOSITION OF FOODS—ANALYSIS OF FOODS—ADULTERATION OF FOODS.

*Sub-Section A. Different kinds of foods.*

*Questions Proposed:*

1. The determination of the nature of oils used in the preparation of preserved fish.
2. Is it possible and expedient to give a definition of beer and to fix regulations for determining the kinds of brewing materials to be used?
3. Are there any substances used in beers which should be prohibited?
4. Composition of distilled spirits in liquors. Impurities, that can be detected and determined therein; the determination of higher alcohols, aldehydes, essences. Composition of the essence of absinthe and its determination.
5. Chemical investigation of bread for the special purpose of determining whether other than wheat flour has been used therein.
6. General method of determining starch in compounded foods.
7. The use of antiseptics for preserving food; the natural presence of antiseptics in certain foods; methods of analysis.



*Sub-Section B. Dairy Products.**Questions Proposed:*

1. Importance and causes of variations in the composition of milk.
2. Classification and characters of the nitrogenous substances in milk.
3. The influence of heat and modification of the properties of the essential elements of milk.
4. The value of chemical and physical examination in determining the adulteration of milk.
5. Methods of establishing milk standards for control purposes. (Pure samples of milk as a means of comparison.)
6. The meaning of the presence of nitrites in milk.
7. Should a minimum content for one or several of the constituents of milk be established?
8. What are the best means for preventing the mixing of skimmed milk with pure milk?
9. Practical methods for exercising control over the sale of milk in cities.
10. Importance and causes of variation in the composition of butter and in the physical and chemical characters of the fat of milk.
11. The value of chemical and physical data in determining the adulteration of butter.
12. Methods of establishing standard butter samples (pure samples as a means of comparison).

## SECTION V.

## POTABLE WATERS.

*Questions Proposed:*

1. Methods of determining iron and manganese in water. Method of removing them from potable waters.
2. The use of ozone and ultraviolet rays for sterilization of potable waters.
3. Comparative results obtained from submerged and non-submerged filters.
4. Patent mineral waters, lemonades, etc.
5. The steps desirable to control their manufacture and sale.

## SECTION VI.

## LEGISLATION REPRESSION OF FRAUDS INSPECTION STATISTICS.

*Questions Proposed:*

1. The legal basis for intervention of public authorities in commerce in foodstuffs.
  - a. Food legislation in different countries.
  - b. A study of the penal systems in vogue for the repression of frauds in foods.
2. The unification of food legislation in different countries. Can it be realized? Is it desirable? What would be the best means of obtaining and continuing recognition of international agreements?
  - a. Construction of an international codex containing legal definitions of purity of food. What would be the advantages or disadvantages of such definitions? In what cases is it desirable to keep in mind the origin of foods in definitions?
  - b. The adoption of an international code regulating legal methods of analysis of foods, for the purpose of stopping frauds and adulterations.
3. Methods respecting inspection of dairies and milk:
  - a. By public authorities. State or towns.
  - b. By means of public institutions.
  - c. By the producers themselves, in the establishment of societies for securing the production and sale of pure and wholesome milk.
4. Can the seller be held responsible for the effects of disease due to the presence of pathogenic germs in the food sold by him?

## SECTION VII.

Inspection of a popular character concerning rational feeding and alimentary hygiene—coöperative societies, food administration, the food of charitable institutions, food in its different sociological relations.

*Questions Proposed:*

1. The working man's food: What is it? Its price in large centers. What is its nutritive value?
  2. International organization of fisheries as a means of obtaining food at low prices.
  3. Is the preservation of meat by refrigeration advantageous? What is the best means of preserving meat? What is the best organization of slaughter-houses?
  4. Desirability of studying the changes of diet that certain classes of working men undergo when leaving one condition in one country for another, socially and physically (moving from the country to the towns; emigration from one country to another, etc.).
  5. The classification of professions as regards outlay of energy; should it be revised especially as regards the working man? Food of working men not only in regard to expenditure of physical strength, but also in regard to their intellectual work.
  6. Food law administration; coöperative societies of consumers; the food bakeries, restaurants, their conduct, their social importance; services rendered to hygiene.
- In what manner should the public authorities exercise control over the above institutions and in what cases should they be encouraged?
7. The teaching of alimentary hygiene and rational feeding in schools, and especially in large cities; the teaching of alimentary hygiene and rational feeding in other places than schools.
  8. Food aid for children and old people.

In acceding to the request for coöperation in this work please signify the section in which you desire to be enrolled, and also on what one or more of the subjects you will prepare a paper.

The above-named problems are of the greatest interest and it is hoped that all persons in this country engaged in their study may take an active part in securing the proper representation from the United States in the Congress.

The membership fee is twenty (20) francs. Relatives of members are entitled to the privileges of associate members on the payment of ten (10) francs. Intending members may send their subscription directly to the Brussels office, addressing M. Grognaud, General Secretary of the Congress, 3 Rue de Louvain, Brussels, Belgium, or to Mr. Sterckx, Treasurer, Chief of Division, Minister of the Interior and of Agriculture, Brussels. If preferred, intending members may send their check (four dollars) to me at the address given below, and I will forward it to Brussels. The difference between the four dollars and the twenty francs will be used in paying the expenses of postage, etc., of the American Committee.

Respectfully,

H. W. WILEY,  
Cosmos Club, Washington, D. C.

## NOTICE.

*Members of the Division of Industrial Chemists and Chemical Engineers:*

To aid in the preparation of a descriptive list of the registered members of the section, the individual members are asked to send to me information covering the following points: Name, address, present position (with title, and name and nature of business of organization with which you are affiliated), lines of chemical industry on research in which you are particularly interested or in which you have had most intimate associa-

tion. If you now hold an official position with the American Chemical Society, either in the local section or the main society, kindly mention that also. The descriptions as they will appear in the directory of the Division must necessarily be concise; therefore try to give the essential information in as condensed form as possible.

Any member of the Society upon request to the Secretary of the Division will be registered as a member of the Division.

F. E. GALLAGHER, *Secretary*,  
93 Broad Street, Boston, Mass.

#### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The name of Louis A. Olney should be added to the Executive Committee of the Division, so that the committee consists of the following members:

##### Executive Committee:

W. H. WALKER,  
J. D. HANDY,  
A. S. CUSHMAN,  
C. P. VAN GUNDY,  
L. A. OLNEY,  
W. D. RICHARDSON, *ex-officio*.  
Yours truly,  
W. D. RICHARDSON.

[The following part of the report of the Committee on Potash, Division of Fertilizer Chemists, was omitted from the February number, THIS JOURNAL, page 71.]

#### POTASH WORK FERTILIZER DIVISION A. C. S., DECEMBER, 1909.

##### Selected Samples,

Analyst	Method					Per cent. gain
	No. 1	No. 2	No. 3	No. 4	No. 2.	
J. Frank Morgan	6.32	6.21	6.40	6.08	....	....
No. 1724	6.41	6.19	6.37	6.06	....	....
P. K. Nisbet, A. A. C. Co.	9.87	10.04	9.91	....	....	0.17
Bradley Works	6.90	6.98	6.84	....	....	0.08
F. B. Forte	10.20	10.33	10.16	....	....	....
	10.11	10.41	10.31	....	....	....
Atlanta, Swift & Co.	10.11	10.37	10.13	....	....	....
Av.	10.15	10.37	10.17	....	....	0.22
R. Henry, V. C. C. Co.	6.45	6.58	6.45	....	....	0.13
G. Earnham, Jarecki Chem Co.	3.61	3.89	3.80	....	....	0.28
J. E. Breckenridge, No. 1.	9.62	10.08	....	....	....	0.46
No. 2.	8.58	8.56	....	....	....	....
A. A. C. Co., No. 3.	7.56	7.93	....	....	....	0.37
No. 4.	4.70	5.03	....	....	....	0.33
No. 5.	6.71	7.10	....	....	....	0.39

##### REMARKS.

F. B. Porter, Swift & Co., Atlanta, Ga.:

Actual water-soluble potash added, 10.57 per cent.; 247-gram sample made up in laboratory, accurately weighing the potash and acid phosphate. Results on this sample agree in general with our previous results published in May, 1909, THIS JOURNAL, but do not show as high a percentage of loss of potash as we have found in other samples.

We favor Method No. 2 as being the best method for water-soluble potash we have so far tried.

J. E. Breckenridge, A. A. C. Co., Carteret, N. J.:

Sample No. 4 was actual weights of acid phosphate, having about 5 per cent. iron and aluminum, and muriate of potash. Theory, 5.17 per cent. water-soluble potash.

#### RECENT INVENTIONS.

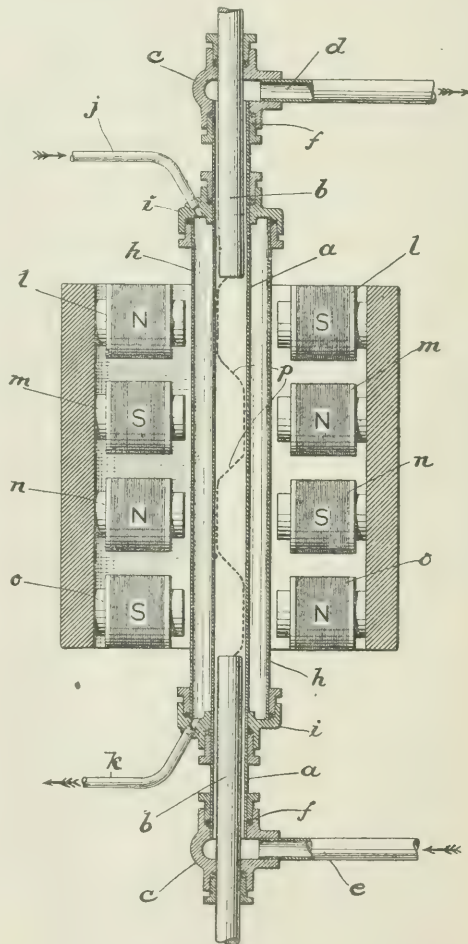
The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Patents, McGill Building, Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

943,661. Production of Oxids of Nitrogen from the Air. F. I. DU PONT. Patented Dec. 12, 1909.

This is an improvement upon the inventor's prior process of producing oxids of nitrogen which consists in subjecting air, in contact with a cooling medium, to the action of a moving or rotating arc whereby the high heating by the arc is immediately and rapidly reduced. In that case the air passing



through the tube is subjected to the action of an electric arc therein, which is caused to rotate by means of a rotary magnetic field surrounding the tube at one point. The inventor has discovered certain improvements upon this invention which improvements consist in providing a plurality of rotating fields

at different points, the fields being oppositely placed so that the arc not only rotates but is caused to move along the tube and crossing the space in the tube. By this arrangement throughout the passage of the air it is subjected several times alternately to the high heating of the rotating arc and to the cooling of the cooling medium.

In the drawing, *a* is a silica tube within which are the electrodes *b*, connected with a source of current supply, not shown.

*c* is a cap applied to each end of the tube *a*, the upper cap having the passage *d* and the lower cap the passage *e*. Between the cap *c* and tube *a* is a packing *f* to hermetically seal the connection at that point. The electrodes *b* are hermetically sealed with respect to the cap. The electrodes are provided with proper feeding mechanism. The cap *c* is such that one portion of the cap closely surrounds the tube *a* and another portion closely surrounds the electrodes. Between these two portions of the caps *a* are, respectively, the passages *d* and *e* which connect with the space between the inner wall of tube *a* and the electrodes *b*. The tube *a* is surrounded by a tube *h*, preferably formed of glass in order to see the operation within the tube *a*. The ends of this tube *h* are closed by the caps *i*, one cap having the inlet opening *j* and the other the outlet *k* for the circulation of the cooling medium.

Surrounding the tube *h* between the electrodes *b* are a series of field magnets or rings *l*, *m*, *n* and *o*, which are energized by a polyphase current or currents, thus producing rotating magnetic fields. These field magnets are arranged as shown so that the poles N and S are alternately placed. This causes the arc formed between the electrodes not only to rotate but to pass from side to side of the tube, as shown at *p* in the drawing.

In operation, the air is forced through the passage *e*, into the zone between the electrodes. When the arc is produced and the rotary magnetic fields in action, the arc is caused to rotate and to be blown from side to side of the tube. This spreads the arc in the tube. By this arrangement, the air will surely have to pass through the arc as many times as the arc crosses over the tube and between passages is cooled by contact with the surrounding cooling medium as in my hereinbefore-mentioned previous application.

The produced oxides of nitrogen, which are the lower oxides of nitrogen, pass into the space between the electrodes and the wall of the tube, escaping by the passage *d*, from which they may be led into water where they are converted into nitric acid in the ordinary manner.

945,926. Smelting Sulphur Ores. RICHARD FLEMING. Patented January 11, 1910.

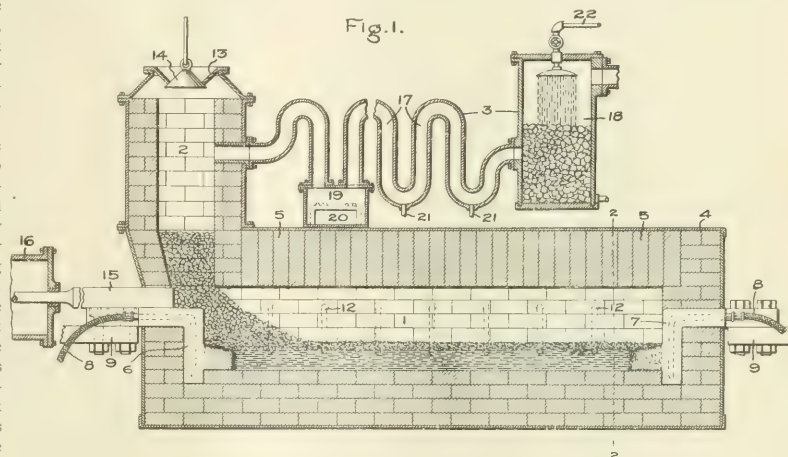
This invention relates to a method of smelting ores containing sulphur. It effects the removal of nearly all of the sulphur, which is recovered as a by-product, and results in the production of a nearly pure metal.

In some of the present methods of smelting these ores the sulphur is burned, and the noxious fumes which escape consti-

tute a serious nuisance in the vicinity of the smelter. This inventor's procedure is designed to not only eliminate this nuisance, but recover a valuable product. Other impurities such as zinc and arsenic are recovered with the sulphur, and are subsequently purified.

The process is carried on in a totally enclosed furnace capable of continuous operation. It is important to carry on the smelting in an enclosed space so as to avoid escape of the vapors, and oxidation of the same. As the walls of the furnace are made relatively thick, it possesses a high heat efficiency, which is especially desirable as the smelting is carried on while the ore is in a fused state. The heat necessary to melt the ore and maintain the same in fusion during the smelting operation is generated in the interior of the furnace by means of electrical energy. This method of heating makes it possible not only to keep the ore out of communication with the atmosphere but enables the highly corrosive melted mass to be confined by thick walls of refractory material.

In the practice of the process when the furnace is charged for the first time the ore may be melted independently and in-

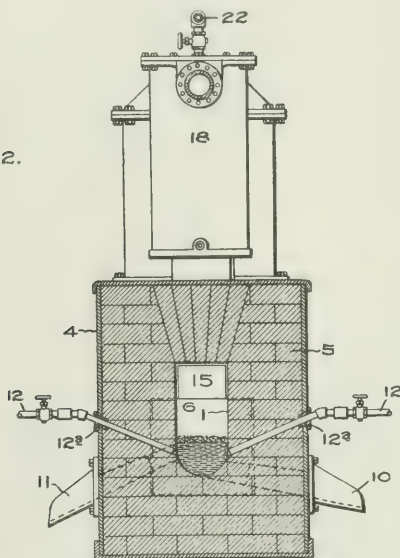


troduced into the furnace in a fused state, if desired, so as to distribute it continuously to the electrodes, or a bar of metal may be placed in the bottom of the furnace from electrode to electrode to serve as a heater, and thus melt the ore which is introduced in the solid state. In either case a continuous conducting layer covering the bottom of the furnace and extending from one electrode to another is to be obtained. In the case of the ores above mentioned, a certain amount of silicious material is introduced with the ore as a flux. This flux combines with the iron to form a slag, as will be later explained. A flow of cooling liquid, as water, is then started through the electrodes and a current sent through the charge. The charge, if not already melted, is liquefied by the heat generated by the passage of the current. The chilled electrode causes a certain amount of the charge to solidify on their surface, as indicated, thus protecting the electrode surface. When the temperature begins to rise, at first considerable sulphur is liberated, the iron pyrites losing one atom of sulphur. Sulphur vapor passes up through the crushed ore in the charging chamber, to which it gives up part of its heat and then passes on into the condensing chamber or dust chamber, where it is condensed. A blast of steam which may be superheated is now introduced into the molten sulphide through the tuyers 12. The steam decomposes the melted sulphids and drives out the



sulphur, at the same time oxidizing the iron to form iron oxid. When sulphid ores, at an elevated temperature, are treated with steam there ordinarily is formed hydrogen sulfid. However, as the temperature is gradually raised an increasing per cent. of hydrogen sulphid is broken up into sulphur and hydrogen. In the vicinity of the temperatures employed in the present process this decomposition is almost complete, and the result of forcing steam into the melted bath results, therefore, in the formation of a certain percentage of hydrogen sulphid, and considerable amounts of sulphur and hydrogen. If desired, a certain amount of air may be forced into the melted sulphid together with the

Fig. 2.



steam, in order to completely oxidize the ores and furnish a certain amount of sulphur dioxide, which will interact with the free hydrogen as well as with the hydrogen of the hydrogen sulphide. Sulphur dioxide will interact with hydrogen and with hydrogen sulphid to form sulphur and water.

As the reactions take place in the melted bath at high temperature they proceed rapidly. The sulphur vapor, watery vapor, together with vapors of other substances associated with the copper, such as arsenic and zinc, are carried off and condensed in the condensing chamber.

The accompanying illustration shows the patentee's furnace.

946,688. Apparatus for Production of Zinc Oxid. W. and H. SIMM. Patented, January 18, 1910.

This invention consists in an apparatus for the rapid production of zinc oxid from zinc ores such as calamins and metallic substances containing zinc.

In operating the apparatus, a furnace setting is first wheeled into position under the hoods 19 and the necessary electrical connections made. The carbon electrodes of the furnace are then connected by a layer of powdered charcoal preparatory to starting the furnace. The effect of this is to obtain an incandescent bed immediately the current is switched on and the charcoal slightly pressed down. The charge can then be fed directly into a live furnace by which the efficiency of the apparatus is increased. The charge is prepared by mixing the ore or other substances containing the zinc in a broken-up state with such materials as salt cake or common salt and slaked lime or with borate of lime. The mixture comes into

the furnace through the hopper 26 and immediately comes into contact with a large surface of incandescent carbon, by which the zinc is immediately volatilized. The volatilization of the zinc is quickened by suitably varying the proportions of the ingredients of the flux used and the greatest efficiency is thus more evenly maintained. The relative proportions of the salt cake or common salt to the lime can be advantageously varied from five to two to about equal proportions according to the quality of the material to be treated and with a given strength of current the voltage can be advantageously kept as high as possible. The proportions of the flux to the material treated will vary from two and a half to twenty-five per cent., according to the character of the said material. The fan 30

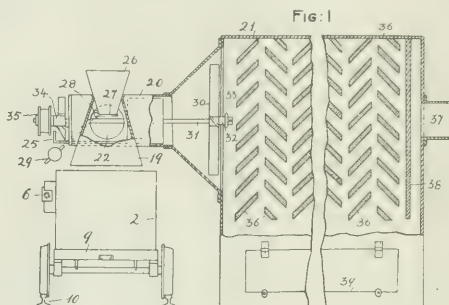
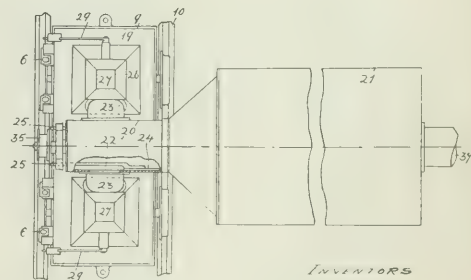


Fig 2



projects the zinc vapor against the baffles or bars 36, by which it is thrown down, and it can then be collected at the door 39. Any other vapors resulting from the reduction of the material containing the zinc are blown out at the orifice 37 and the clearing out of the condenser of such foreign vapors can be facilitated by the use of a suction fan at the outlet orifice as before stated.

946,903. Electrolyte and Method of Electrodepositing Copper. EDWARD F. KERN. Patented January 18, 1910.

The patentee has discovered that a smooth, dense, coherent and adherent deposit of copper may be obtained by the electrolysis of a bath containing fluosilicate of copper in solution and that particularly good results may be obtained by the use of a soluble alkaline or alkaline-earth fluosilicate, preferably ammonium fluosilicate, or in some cases aluminium fluosilicate, with the copper fluosilicate, and that the operation may be further improved in some cases by the additional employment of an alkaline fluoride as ammonium fluoride either alone or with an organic salt, preferably an alkaline tartrate.

For coating iron, steel or zinc, the following materials are employed:

Water	100 parts
Copper fluosilicate	12 parts
Ammonium fluosilicate	8 parts
Ammonium tartrate	6 parts
Ammonium fluorid	5 or more parts

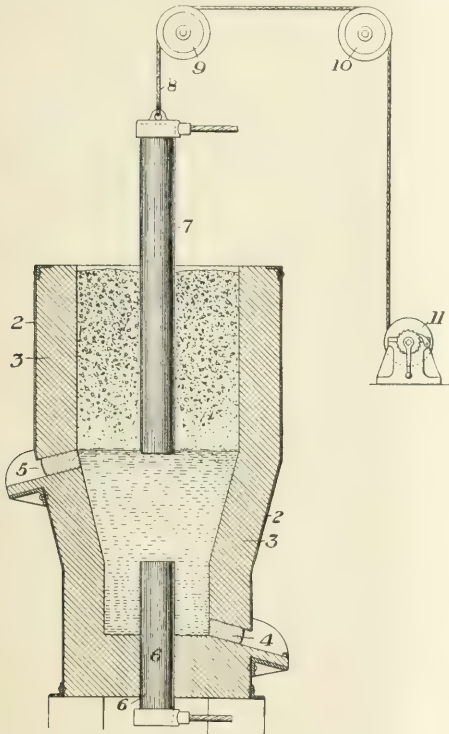
For coating brass, copper or certain other metals, the following materials are used:

Water	100 parts
Copper fluosilicate	12 parts
Ammonium fluosilicate	8 parts
Gelatine or tannin	0.06 part
Ammonium fluorid	5 or more parts

**947,723. Reduction of Scruff and Dross.** RAYMOND S. WILE. Patented January 25, 1910.

This invention relates to the reduction of scruff and dross from tinning, galvanizing and similar operations, and is designed to provide a method which will eliminate loss of metal and work rapidly and cheaply.

In carrying out the method the patentee employs an electric furnace, and uses in conjunction therewith some form of carbon which will unite with the oxygen of the oxide in the dross or scruff under the electrically developed heat. He also em-



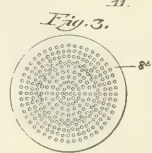
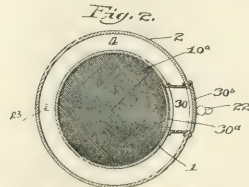
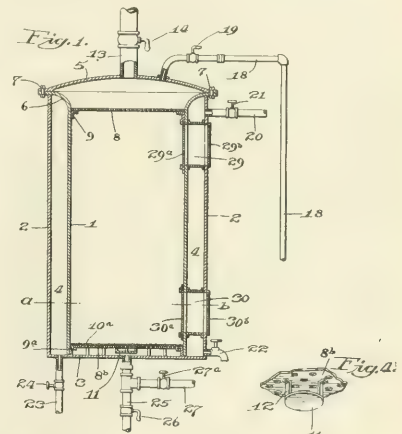
employs in the lower portion of the furnace a well or body of neutral melted material, such as glass, within which the reduced metal descends, thus protecting it from oxidation, and enabling the globules to collect so that the metal may be tapped out.

The scruff, or dross, or both, is preferably mixed with some form of carbon, such as coke dust, and this mixture is fed into the furnace and lies on the top of the glass bath. Under the heat received by this mixture through conduction and radia-

tion, the carbon unites with the oxygen of the metal oxides, thus reducing them to the metal, as the charge descends within the furnace. This reduction takes place during the descent through the successively higher zones of heat, and the reduced metal passing through the layer of coke on the glass which performs the final reduction (if the added coke is used) enters the glass bath and descends and collects therein. This neutral bath protects the globules against oxidation, and assists them in uniting to form a body of molten metal which collects around the lower electrode, and may be tapped out from time to time through the lower tap hole. Successive charges of the mixture may be fed in from time to time.

**947,503. Process of Purifying Animal Charcoal and the Product Thereof.** JOHN HENRY UTLEY. Patented January 25, 1910.

This invention relates to the purification of animal charcoal or bone-black to prepare it for use in the industrial arts as an agent for clarifying and decolorizing gelatin and glue liquors, sugar and glucose solutions, and the like. When so employed it is comminuted, or at least ground, to a granulated condition of fineness; in character it is porous and hence highly absorbent, but there are two objections to its use, first because of calcium phosphate and perhaps other mineral salts and impurities, combined with it, and hence it is not in its highest state of efficiency initially, and when once used for the purpose stated



it loses much of its porous character, taking on an apparent change of composition, due largely, if not wholly, to absorption of salts and acids from the gelatine liquor or other liquid clarified and decolorized by it, and is thereby rendered wholly inefficient, in such condition, for a repetition of the process, but capable of being revived, as it is called, which is a troublesome and expensive method, commonly effected by a washing of the spent charcoal followed by a reburning of it.

This invention has two objects in view, principally the restoration or revivification of such spent animal charcoal, and

incidentally the treatment of it, in its initial state, to render it more efficient—my process, about to be described, fully effecting both objects by the same steps, acting successively on the same body of animal charcoal in its initial and spent conditions, respectively, or on the latter only if the first application is not deemed essential or desirable for the particular liquid material to be clarified and decolorized.

To these ends the invention consists in the discovery that if a body of animal charcoal of commerce, ground to a granulated condition and confined in a substantially closed vessel with suitable inlet and outlet apertures to connect steam and water pipes thereto, is subjected to the action of a column of live steam blown through it, followed preferably by a washing with a volume of hot water, driven preferably in the opposite direction, through the container vessel, that the animal charcoal will not only be deprived of deleterious impurities, but the steam will deprive it, by chemical action perhaps, of its combined salts, which have never heretofore been removed from it; and that ground animal charcoal, so prepared for use as a clarifying and decolorizing medium, is not only more efficient as such, but what is of greater value, the charcoal, after such use, can be perfectly restored and revived by a repetition of the same steps, thereby wholly saving the labor and expense of washing and reburning it as now commonly practiced.

The accompanying illustration shows an apparatus in which the patentee's process is practiced.

## OFFICIAL REGULATIONS AND RULINGS.

Only a few of the more important rulings are reported here. For others the reader is referred to the publications of the Board of Food and Drug Inspection and to Treasury Decisions.

### FOOD INSPECTION DECISION 112.

#### *Amendment to Regulation 28 (Labeling of Derivatives)*

Section 8 of the Food and Drugs Act of June 30, 1906, paragraph "Second," under "Drugs," provides that a drug shall be deemed to be misbranded "if the package fail to bear a statement on the label of the quantity or proportion of any alcohol, morphine, opium, cocaine, heroin, alpha or beta eucaine, chloroform, cannabis indica, chloral hydrate, or acetanilide, or any derivative or preparation of any such substances contained therein."

In an opinion rendered January 15, 1909, the Attorney-General held that a derivative within the meaning of this section of the act is a substance which is so related to one of the specified substances "that it would be rightly regarded by recognized authorities in chemistry as obtained from the latter 'by actual or theoretical substitution,' and it is not indispensable that it should be actually produced therefrom as a matter of fact;" and, further, that the labeling of derivatives, as prescribed by this section, is a proper subject conferred upon them by Section 3, and that a rule or regulation requiring the name of the specified substance to follow that of the derivative would be in harmony with the general purpose of the act, and an appropriate method by which to give effect to its provisions.

In conformity with this opinion, the Board of Food and Drug Inspection recommends that Regulation 28 of the Rules and Regulations for the enforcement of the Food and Drug Act, published in Circular 21 of the Office of the Secretary, be amended by the addition, to follow paragraph (j), of a new paragraph to be designated as paragraph (g), reading as follows:

(g) In declaring the quantity or proportion of any of the specified substances the names by which they are designated in the act shall be used, and in declaring the quantity or proportion of derivatives of any of the specified substances, in addition to the trade name of the derivative, the name of the

specified substance shall also be stated, so as to indicate clearly that the product is a derivative of the particular specified substance.

This paragraph (g) prescribes, in effect, that in labeling derivatives the name of the specified substance must be stated, so as to clearly indicate that the product is a derivative of the particular substance named in the act.

Regulation 28 as amended shall be effective on and after April 1, 1910, and the regulation in full shall read as follows:

#### *Regulation 28.—Substances Named in Drugs or Foods.*

(Section 8, second under "Drugs;" second under "Foods.")

(a) The term "alcohol" is defined to mean common or ethyl alcohol. No other kind of alcohol is permissible in the manufacture of drugs except as specified in the United States Pharmacopoeia or National Formulary.

(b) The words alcohol, morphine, opium, etc., and the quantities and proportions thereof, shall be printed in letters corresponding in size with those prescribed in Regulation 17, paragraph (c).

(c) A drug, or food product, except in respect of alcohol, is misbranded in case it fails to bear a statement on the label of the quantity or proportion of any alcohol, morphine, opium, heroin, cocaine, alpha or beta eucaine, chloroform, cannabis indica, chloral hydrate, or acetanilide, or any derivative or preparation of any such substances contained therein.

(d) A statement of the maximum quantity or proportion of any such substances present will meet the requirements, provided the maximum stated does not vary materially from the average quantity or proportion.

(e) In case the actual quantity or proportion is stated it shall be the average quantity or proportion with the variations noted in Regulation 29.

(f) The following are the principal derivatives and preparations made from the articles which are required to be named upon the label:

ALCOHOL, ETHYL (Cologne spirits, grain alcohol, rectified spirits, spirits, and spirits of wine):

#### *Derivatives—*

Aldehyde, ether, ethyl acetate, ethyl nitrite, and paraldehyde.

#### *Preparations containing alcohol—*

Bitters, brandies, cordials, elixirs, essences, fluid extracts, spirits, sirups, tinctures, tonics, whiskies, and wines.

MORPHINE, ALKALOID:

#### *Derivatives—*

Apomorphine, dionine, peronine, morphine, acetate, hydrochloride, sulphate, and other salts of morphine.

#### *Preparations containing morphine or derivatives of morphine—*

Bougies, catarrh snuff, chlorodyne, compound powder of morphine, crayons, elixirs, granules, pills, solutions, sirups, suppositories, tablets, triturations and troches.

OPIUM GUM:

#### *Preparations of opium—*

Extracts, denarcotized opium, granulated opium, and powdered opium, bougies, brown mixture, carminative mixtures, crayons, dower's powder, elixirs, liniments, ointments, paregoric, pills, plasters, sirups, suppositories, tablets, tinctures, troches, vinegars, and wines.

#### *Derivatives—*

Codaine, alkaloid, hydrochloride, phosphate, sulphate, and other salts of codaine.

#### *Preparations containing codaine or its salts—*

Elixirs, pills, sirups, and tablets.



**COCAINE, ALKALOID:***Derivatives—*

Cocaine hydrochloride, oleate, and other salts.

*Preparations containing cocaine or salts of cocaine—*

Coca leaves, catarrh powders, elixirs, extracts, infusion of coca, ointments, paste, pencils, pills, solutions, sirups, tablets, tinctures, troches, and wines.

**HEROIN:***Preparations containing heroin—*

Sirups, elixirs, pills, and tablets.

**ALPHA AND BETA EUCAINE:***Preparations—*

Mixtures, ointments, powders, and solutions.

**CHLOROFORM:***Preparations containing chloroform—*

Chloranodyne, elixirs, emulsions, liniments, mixtures, spirits, and sirups.

**CANNABIS INDICA:***Preparations of cannabis indica—*

Corn remedies, extracts, mixtures, pills, powders, tablets, and tinctures.

**CHLORAL HYDRATE (Chloral, U. S. Pharmacopoeia, 1890):***Derivatives—*

Chloral acetphenonoxim, chloral alcoholate, chloralamide, chloralimide, chloral orthoform, chloralose, dormiol, hypnal, and uraline.

*Preparations containing chloral hydrate or its derivatives—*

Chloral camphorate, elixirs, liniments, mixtures, ointments, suppositories, sirups, and tablets.

**ACETANILIDE (Antifebrine, phenylacetamide):***Derivatives—*

Acetphenetidine, citrophen, diacetanilide, lactophenin, methoxy-acetanilide, methylacetanilide, para-iodoacetanilide, and phenacetine.

*Preparations containing acetanilide or derivatives—*

Analgesics, antineuralgics, antirheumatics, cachets, capsules, cold remedies, elixirs, granular effervescent salts, headache powders, mixtures, pain remedies, pills, and tablets.

(g) In declaring the quantity or proportion of any of the specified substances the names by which they are designated in the act shall be used, and in declaring the quantity or proportion of derivatives of any of the specified substances, in addition to the trade name of the derivative, the name of the specified substance shall also be stated, so as to indicate clearly that the product is a derivative of the particular specified substance.

H. W. WILEY,

F. L. DUNLAP,

GEO. P. McCABE,

*Board of Food and Drug Inspection.***Approved:**

FRANKLIN MACVEAGH,

*Secretary of the Treasury.*

JAMES WILSON,

*Secretary of Agriculture.*

CHARLES NAGEL,

*Secretary of Commerce and Labor.*

WASHINGTON, D. C., January 6, 1910.

**NOTICE OF JUDGMENT, 130, FOOD AND DRUGS ACT.***Adulteration and Misbranding of Lemon Extract.*

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of Regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 9th day of June, 1909, in the Circuit Court of the United States for the eastern district of Louisiana, in a prosecu-

tion against Albert Mackie Grocer Company (Limited), a corporation of New Orleans, La. (F. & D. No. 482), for violation of Section 2 of the aforesaid act in shipping and delivering for shipment from Louisiana to Mississippi, an adulterated and misbranded lemon extract, the said Albert Mackie Grocer Company (Limited) entered a plea of guilty, whereupon the Court imposed upon it a fine of \$10 and costs of the prosecution.

The facts in the case were as follows:

On April 7, 1908, an inspector of the United States Department of Agriculture purchased from N. B. Whalen, McComb City, Miss., a sample of lemon extract, labeled "McE. Brand Flavoring Extract of Lemon. Albert Mackie Grocer Co., Ltd., New Orleans, La.," which had been manufactured and shipped by the Albert Mackie Grocer Company (Limited), from New Orleans, La., to the said dealer on or about August 15, 1907. The sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture, and the following results obtained and stated:

Specific gravity (15.5° C.).....	0.9614
Alcohol by volume (per cent.).....	34.35
Solids (grams per 100 cc.).....	0.46
Lemon oil (by polarization) (per cent.).....	0.5
Lemon oil (by precipitation).....	None
Color.....	Coal tar

Lemon extract, as recognized by the Department of Agriculture and reputable manufacturers in the United States, is the flavoring extract prepared from oil of lemon or from lemon peel, or both, and contains not less than 5 per cent. by volume of lemon oil.

It was evident that the product was both adulterated and misbranded within the meaning of Sections 7 and 8 of the act; adulterated, because a substance had been substituted in whole or in part for oil of lemon, and because it was an imitation extract colored with a coal-tar dye to give it the color of genuine lemon extract, thereby concealing inferiority; and misbranded, because labeled "Extract of Lemon," whereas it was not lemon extract.

The Secretary of Agriculture having, on September 30, 1908, afforded the manufacturers an opportunity to show any fault or error in the aforesaid analysis, and they having failed to do so, the facts were reported to the Attorney-General and the case referred to the United States attorney for the eastern district of Louisiana, who filed an information against the Albert Mackie Grocer Company (Limited), with the result hereinbefore stated.

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., January 10, 1910.

*Adulteration of Milk.*

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of Regulation 6 of the rules and regulations for the enforcement of the act, notice is given of the judgments of the Court in the cases of the United States *vs.* M. Boyle (F. & D. No. 439), United States *vs.* C. E. Williams (F. & D. No. 440), and United States *vs.* J. C. Kotzenberg (F. & D. No. 441), prosecutions lately pending in the District Court of the United States for the eastern district of Wisconsin for violations of Section 2 of the aforesaid act in the shipment from Wisconsin to Illinois by the aforesaid defendant, M. Boyle, of milk which was adulterated within the meaning of Section 7 of the act, in that water had been mixed with, and substituted in part for, the milk, thereby lowering and reducing its quality and strength; and in the shipment by the aforesaid defendants, Williams and Kotzenberg, from Wisconsin to Illinois, of milk which was adulterated within the meaning of Section 7 of the act, in that cream, a valuable constituent thereof, had been abstracted therefrom. On June 26, 1909, the defendant, M. Boyle, having been arraigned upon an information alleging

the aforesaid shipment by him of adulterated milk, entered his plea of guilty and was sentenced by the Court to pay a fine of \$25. On April 16, 1909, the defendants, C. E. Williams and J. C. Kotzenberg, having been arraigned upon information alleging the aforesaid shipments by them of adulterated milk, entered their pleas of guilty and were sentenced by the Court to pay a fine of \$25 each and stand committed to jail until such fine should be paid.

These cases were based upon samples of milk procured by inspectors of the United States Department of Agriculture on August 28, 1908, from the shipping cans after the milk had reached Chicago from the respective consignees and points of shipment, namely, M. Boyle, Woodworth, Wis.; C. E. Williams, Genoa Junction, Wis.; and J. C. Kotzenberg, Bassett, Wis., for delivery to J. H. Tyley, F. Deitmer, and Theodore Renz, respectively. The inspectors saw the said several shipments of milk delivered to the railroads at the points of shipment, identified each shipment with its consignor, and accompanied them to Chicago. The aforesaid samples were duly analyzed in the Bureau of Chemistry of the United States Department of Agriculture, and it was found that those taken from the milk shipped by the said Williams and Kotzenberg contained, respectively, an average of a little less than 8.70 per cent. of solids-not-fat and 2.6 per cent. of milk-fat, and 8.50 per cent. of solids-not-fat and 2.6 per cent. of milk-fat, indicating that the milk had been skimmed and that those taken from the milk shipped by said Boyle contained a little less than 7.36 per cent. of solids-not-fat and 3.1 per cent. of milk-fat, indicating that water had been added to the milk.

It appearing from the aforesaid analyses that the milk was adulterated, the Secretary of Agriculture gave notice to the respective parties and gave them an opportunity to be heard, but the said parties having failed to show any fault or error in the result of the said analyses and it being determined that the milk was adulterated, the said Secretary, on February 17, 1909, reported the facts and evidence to the Attorney-General, by whom they were referred to the United States attorney for the eastern district of Wisconsin, who filed informations against the aforesaid defendants, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., January 10, 1910.

(N. J. 133.) *Adulteration and Misbranding of Olive Oil.*

(A Mixture of Cottonseed and Olive Oils.)

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of Regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 15th day of June, 1909, in the Circuit Court of the United States for the eastern district of Louisiana, in a prosecution by the United States against King Brothers, Shilstone & Saint (Limited), a corporation of New Orleans, La. (F. & D. No. 295), for violation of Section 2 of the aforesaid act in shipping and delivering for shipment from Louisiana to Texas an article of food labeled "Balbiani & Cie. Huile d'Olive Superfine Raffinee," which was adulterated and misbranded within the meaning of Sections 7 and 8 of the act, the said defendant having entered a plea of guilty, the Court imposed upon it a fine of \$10 and costs.

The facts in the case were as follows:

On January 28, 1908, an inspector of the Department of Agri-

culture purchased from Ullman, Stern & Krausse, Galveston, Tex., a sample of oil contained in bottles upon the principal label of which was printed "Balbiani & Cie. Huile d'Olive Superfine Raffinee," and upon a supplemental label, "This product is a compound of salad oil and imported olive oil, packed by King Bros., Shilstone & Saint, Ltd., New Orleans, La." On the back of each bottle was a label printed in Italian, French, and English to the effect that the oil of the new firm of Balbiani & Cie was guaranteed free from mixture. This sample was part of a shipment made on or about October 29, 1907, by the manufacturers, King Brothers, Shilstone & Saint (Limited), from New Orleans, La., to said Ullman, Stern & Krausse. The sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture, and the following results obtained and stated:

Specific gravity 15.5° C	0.9207
Index refraction 15.5° C	1.4751
Iodine number	104.89
Halphen test	Positive
Villavechia test	Negative
Renard test	Negative
Adulterant	Cottonseed oil

It was evident from this analysis that the article was a mixture of cottonseed oil and olive oil, the former predominating. It was therefore adulterated within the meaning of Section 7 of the act, in that cottonseed oil had been substituted in part for olive oil, which it purported to be, and cottonseed oil had been mixed with olive oil so as to reduce its quality and strength, and was misbranded within the meaning of Section 8 of the act, in that the statements and representations on the labels that it was olive oil and a foreign and imported article produced by a foreign company, Balbiani & Cie, and guaranteed free from mixture, were false, misleading and deceptive. The statement on the supplemental label that the product was packed by King Brothers, Shilstone & Saint (Limited) did not cure the false, misleading and deceptive character of the principal and secondary labels, since the packing of the oil by King Brothers, Shilstone & Saint could not be inconsistent with the representation that the oil was produced in a foreign country by a foreign company, nor was the statement on the label that it was a compound of salad oil and imported olive oil true, because the usual acceptance of the term "salad oil" does not include cottonseed oil.

It appearing from the aforesaid analysis that the article was adulterated and misbranded, the Secretary of Agriculture gave notice to Ullman, Stern & Krausse, the dealer from whom the sample was purchased, as well also as to the manufacturer and shipper, King Brothers, Shilstone & Saint (Limited), and gave them an opportunity to be heard. King Brothers, Shilstone & Saint being the party solely responsible for the adulteration and misbranding of the article and failing to show any fault or error in the result of the aforesaid analysis, and it being determined that the article was adulterated and misbranded, on December 30, 1908, the said Secretary reported the facts and evidence to the Attorney-General, by whom they were referred to the United States attorney for the eastern district of Louisiana, who filed an information against the said King Brothers, Shilstone & Saint, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., January 10, 1910.

# THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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APRIL, 1910.

No. 4

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## ORIGINAL PAPERS.

### LUBRICATION AND LUBRICANTS.

By CHARLES F. MAHERY, Professor of Chemistry, Case School of Applied Science.

Received January 25, 1910.

Next to the conservation of the world's fuel supply there is probably no subject of greater importance in the manufacturing world than the control of waste power caused by imperfect lubrication and needless friction. Notwithstanding the increasing interest in more economical methods the immense losses from this source are scarcely appreciated. In his recent work on lubrication and lubricants Archbutt stated that of the 10,000,000 h. p. in use in the United Kingdom of Great Britain considerably more than half this amount, 40 to 80 per cent. of the fuel, is spent in overcoming friction, and that a considerable proportion of this power is wasted by imperfect or faulty lubrication. On account of the great abundance of cheap fuel in the United States, doubtless the conditions here are even less desirable. It is safe to state that losses from this source in this country are from 10 to 50 per cent. of the power employed. Not infrequently in factories where the annual expense for lubrication amounts to thousands of dollars, lubrication experts find a loss of 50 per cent. or greater.

The manufacturer often knows very little concern-

ing the economic qualities of the lubricants he receives; in using them too much is left to "rule of thumb" methods with little knowledge of the actual conditions of friction, the action of metallic surfaces under the dynamic stress of the transference of power, or such modified action as is produced by the intervention of a lubricating film. For example, the different effects on a journal of a soft and hard bearing may be sufficient to cause a considerable loss of power, if improperly selected, and yet escape attention. In the earlier tentative study of the conditions depended on for the results described in this paper, under such loads as 100, or 150 lbs. per sq. in. of bearing surface, the grades of babbitt in ordinary use were found much too soft and yielding to sustain such work under the necessary conditions of speed and oil feed; only a very hard alloy of exceptional composition could be used; the one selected of approximately the composition tin 90, copper 2, antimony 8 gave results entirely satisfactory. Then since it was desired to maintain such conditions of load and speed that any oil could be broken down at any moment, it was found to be necessary, not only that the journal and bearing be milled to mechanically true surfaces, but that by continued operation and repeated careful milling even a higher degree of permanent evenness be maintained. If such be the essential conditions in precise quantitative observations, similar precautions are evidently necessary in factory operations.

In the earlier days of machinery lubrication before the introduction into the trade of products from petroleum, the manufacturer had little concern about viscosity and other physical constants of lubricants, for dealing with simple oils or greases of definite composition, he could be sure of obtaining what he desired within the capacity of the materials at his disposal. Then, in the days of higher prices of manufactured products and less severe competition imperfect lubrication was of less consequence than in more recent times when every detail of cost and loss should properly receive careful attention; and, furthermore, the principles of friction and the importance of its control were in the earlier days of lubrication only imperfectly understood. Modern high speeds and excessively heavy loads had not then to be provided for in the applications of power in manufacturing operations, in transmission, or transportation.

The discovery that the heavy hydrocarbons in petroleum possessed the qualities requisite in lubricants—viscosity, durability, stability under varying conditions of speed and load—was the beginning of



a new era in lubrication. Methods of treatment and refining, with little or no knowledge of the hydrocarbons of which the lubricating oils were composed developed entirely along empirical lines, were slow in producing suitable products. The earlier methods have undergone no fundamental changes even to the present time, except in the introduction of heavier hydrocarbons from crude oil territory more recently developed. Crude oils of the Pennsylvania type containing a considerable proportion of the hydrocarbons  $C_n N_{2n+2}$  have always yielded excellent light spindle oils composed for the most part of the hydrocarbons  $C_n H_{2n}$  and  $C_n H_{2n-2}$ . But as we now know this type of oils include too small a proportion of the heavier hydrocarbons for the body necessary in lubricators subjected to the great stress of heavy loads, and cylinder friction. This need in heavy lubrication led to the practice of compounding oils, or mixing with the petroleum products various proportions of the vegetable oils, such as castor or rape, and the various animal oils or greases, which so fully monopolized this field, that manufacturers were often led to believe that no other products could serve an equivalent purpose. Even since the more recent introduction of heavy lubricators from Texas and California petroleum the belief still prevails that only compounded oils can be relied on for heavy work. But with care in distillation and treatment, it is certain that heavy lubricators well adapted for bearings and cylinders may be prepared from those crude oils, and large quantities of such lubricants are now widely in use.

All experimenters with lubricating oils who have given thoughtful attention to the essential needs of lubrication have been impressed by the superiority of an ideal solid lubricant, one that should embody an equivalent of the desirable qualities of the liquid products with a greatly superior wearing quality, a low coefficient of friction, and readily convertible into a form that can conveniently be applied to the various forms of journals and bearings. Soapstone, asbestos, natural graphite, etc., do not, altogether, possess these fundamental qualities of the liquid products. Greases compounded with graphite are useful on low-speed bearings and under heavy work. Natural graphite serves an excellent purpose on cast-iron bearings, acting as a surface evenner of the porous metal. On finer surfaces care is necessary that it does not collect in such quantities as to seriously scratch or abrade the journal and bearing. Of all the solid bodies available for lubrication, graphite possesses the desirable unctuous quality and great durability. For general use in lubrication graphite must be in its purest condition and in a state of extreme subdivision. Whether in such a condition as the deflocculated form, the ultimate molecules or atoms have a certain freedom of movement, analogous

to that of liquid molecules under stress of friction, or whatever explanation may be suggested of its unctuous quality the fact remains that it possesses this quality in very high degree.

Such graphite is now produced by processes discovered, perfected, and placed on a manufacturing basis by Dr. Edward G. Acheson, of Niagara Falls, as a part of his great work in the development of electrochemical processes. Besides his immense output of pure graphite for general commercial use, Dr. Acheson has succeeded in converting it into a new form, a deflocculated condition, that meets the requirements of an ideal solid lubricant. This deflocculated form greatly surpasses ordinary graphite in unctuous quality, and its adaptability for prolonged suspension in water and oils render it especially applicable to frictional conditions. Furthermore, the readiness with which it forms coherent films on journals, its great wearing qualities and the ease of the application, constitute it a lubricant of extremely high efficiency.

Acheson graphite can be produced from any substance that contains carbon in a non-volatile form. Under the extreme temperature of the electric furnace any and all other elements are readily volatilized. Even carbon itself is freely vaporized and its peculiar appearance in the burning carbon-monoxide is depended on as an indicator of suitable conditions in furnace operation, much as the drop in the manganese flame which shows the disappearance of carbon in the Bessemer converter. As commercial products, two forms of graphite are produced, the unctuous and the deflocculated modifications, the first form accompanying the production of carborundum in furnaces charged with carbon and sand, the second obtained from a charge of coal or coke alone. The first form is leafy in structure, coherent, and extremely unctuous or greasy in its feel; it is segregated and not readily disintegrated. The second form is also unctuous, in a high degree, but very pulverulent and capable of extreme subdivision; it is readily converted into a deflocculated condition, and this form in water forms the commercial "Aquadag," or aqueous Acheson deflocculated graphite. In combination with oils it is known as "Oildag."

This deflocculated condition of graphite has peculiar properties; it remains suspended indefinitely in water, but is quickly precipitated by impurities. On account of its extreme subdivision, a very small amount suspended in water serves for efficient lubrication. From numerous and long-continued trials it appears that 0.35 per cent. serves an adequate purpose and that a larger proportion is superfluous. It is certainly remarkable that such a small quantity of graphite is readily distributed by water between a journal and bearing while sustaining a load of 70 lbs. per sq. in. of bearing surface, and that under high-speed con-

ditions it maintains an extremely low coefficient of friction.

Proper lubrication of bearing surfaces involves careful consideration of the metals composing the journal and bearing, since the influence of the metals employed has an effect even in the intervention of the best lubricating film. The materials in common use for the construction of bearings include cast-iron, steel, and alloys of variable composition included under the general terms bronze and babbitt. In high-speed work cast-iron bearings must be used with extreme care. In the accurate adjustment necessary in machine testing of lubricators, we have found it impossible to prevent injury to the journal when using a cast-iron bearing. Results obtained by the use of bronze have not been altogether satisfactory. Properly selected babbitt, however, on a steel journal seems to fulfil the desired conditions most satisfactorily and it possesses a wide range of applicability. As mentioned above, satisfactory lubrication is possible only when the journal and bearing are properly milled to true surfaces, kept smooth, accidental scratches worked out, and bare spots avoided. Successful lubrication demands constant skilled attention to the condition of journals and bearings, and no factory supervision affords more desirable returns. Lubrication consists in reducing friction to the lowest increment of the power in use. A lubricant is an unctuous body that readily forms a continuous, coherent, durable film capable of holding apart rolling or sliding surfaces, and itself interposing the least possible resistance by its own internal friction. The economic problem in lubrication depends on the use of such a lubricant under suitable conditions.

The lubricators in commercial use include water, oils, greases and solids. Under oils is classified the great variety of light spindle, heavy engine and cylinder products, either unmixed hydrocarbons from petroleum or compounded oils—mixture of the petroleum hydrocarbons with some one of the vegetable oils, or with animal oils—tallow, wool grease, etc. The greases may be generally classified under a few heads depending on their consistency which is derived from the proportion of lime or soda soaps or oleates mixed with a hydrocarbon oil as a carrier. The solid greases have already been referred to. Water in itself possesses no oiliness whatever, but under certain conditions in cylinders it is found to assist in imparting to the metallic surfaces an extremely smooth condition which serves to materially reduce the friction. A practical knowledge of hydrocarbon lubricants should include a knowledge of the source; that is, the crude oil from which the lubricant is prepared, since there is a wide difference in composition and properties of the hydrocarbon oils from different oil fields. Methods of refining petroleum oils have very much to do with the quality of the

products. In general terms inferior products are obtained when the process of distillation is conducted in such a way as to produce decomposition; the best products are obtained only by careful distillation and careful treatment in refining, whereby the hydrocarbons in the refined products obtained have essentially the same composition that they had in the original crude oil. An examination of various lubricating oils in the trade frequently reveals a condition of the oils indicating improper refining. For example, it does not need the application of extremely delicate tests to show the presence of free alkali, of sodium sulphate or of sodium salts of organic acids, any one or all of which may be injurious to metallic surfaces. One of the most exacting duties of the refiner is the treatment with caustic soda in such a manner as to remove all acid products and at the same time to avoid such an excess of caustic as will form an emulsion, which is one of the "terrors" in the refinery. An examination of a great variety of oils in the trade such for instance as the spindle oils in use in automobile service indicates that the best refined oils are those that contain a minute trace of alkali.

The ordinary methods of testing lubricating oils include determinations of viscosity, specific gravity, the flash and fire temperatures; another important property of these oils which is termed oiliness or greasiness is not so readily determined by analysis; in fact there seems to be no accurate method for its determination, yet it is readily distinguishable and has much to do with the efficiency of all lubricating oils. Concerning the most efficient methods of testing lubricating oils, various opinions are expressed by different authors. Redwood in his work on petroleum and its products asserted that the viscosity of an oil is the best guide to its lubricating value since it enables the consumer to select oils similar to those that have afforded him the best practical results. He alludes to the close relationship between viscosity and the laws of friction of liquids. In comparing the use of viscosity with observations on the behavior of lubricants on a frictional testing machine he states that he was unable to obtain satisfactory results with any machine at his disposal; his conclusions in general were that in the present state of our knowledge the indications afforded by testing machines are wholly misleading, and this led him to attach special importance to a good system of testing viscosity. He refers to the opinion of Thurston that any oil should be tested on a machine under the conditions of load and speed similar to those of the use for which the oil is intended. Referring to the work of Ordway and Woodbury in 1884 with an apparatus constructed to apply pressures of 40 lbs. per sq. in., and to those of Tower carried on under what he terms great pressures, 100 to 600 lbs. per sq. in. in an oil bath system of lubrication, and opinions of others on these results,

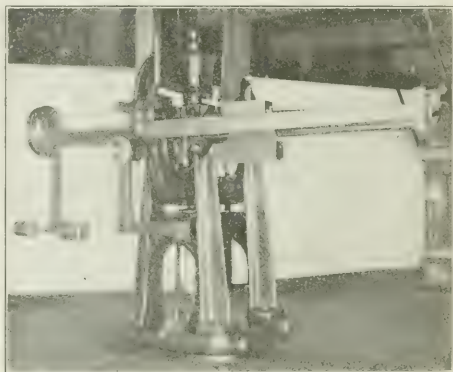
Redwood presents the view that the agreement between machines and actual practice is extremely slight and his final conclusion is that viscosity affords the most valuable tests of lubricating qualities at our disposal. Inasmuch as Redwood's opinion on machine testing is a result of his observations during several months on the Ingram and Stafer machine in which the speed is 1500 r. p. m., and that the friction is gaged by the number of revolutions necessary to carry the temperature to 300° F., it is not difficult to understand his conviction that in his experience testing machines do not afford results comparable with those of actual practice.

The value of viscosity as a distinguishing property of lubricating oils is recognized by all who have given attention to the subject, but all are not agreed as to the extent of its practical reliability. Archbutt suggests that the quality of oiliness or greasiness is nearly of as much importance as viscosity. Although as mentioned above there is no precise method whereby oiliness can be determined, it is not difficult to recognize it nor to distinguish the marked differences in this respect shown by different oils and greases. Archbutt calls attention to the fact that at very low speeds the friction of a cylindrical journal should be proportional to the viscosity of the oil, but at higher speeds and consequently increased temperatures the relation of friction to speed ceases, and the viscosity is diminished with a corresponding change in the carrying power of the journal. While fully appreciating the value of the information to be obtained by chemical analysis, Archbutt insists that the oiliness of a lubricant is of especial importance under heavy loads and high speeds. He suggests that it is advantageous for an engineer to test oils for himself on a machine without depending altogether on analytical data or physical tests obtained from the expert.

Hurst also mentions that a broader knowledge of the practical working of oils is necessary than can be obtained from chemical or physical tests alone. He maintains that the test of an oil from a journal under the practical conditions of its use shows conclusively its adaptability to such use.

The principal points to be observed in mechanical tests are the effects of speed, load, temperature, and the frictional effects due to viscosity and oiliness; the measurements on which depend the quality of the oil include the frictional resistance, the temperatures, and the endurance of the oil film. Doubtless the numerous machines that have been constructed for testing oils have certain merits and advantages. In the wide range of work carried on in this field during the past year, a part of the results of which are presented in this paper, the machine devised by Professor Carpenter has been used. In its sensitive adjustment, durable efficiency, and the wide range of possible tests, this machine in continuous use during

this period on light and heavy oils, greases and graphite has fulfilled all requirements. Since the results to be presented are closely dependent upon the method employed, a view of this machine is here introduced.



Carpenter machine

This machine has an accurate adjustment for recording the speed, and a long lever arm with a vernier attachment graduated to tenths of a pound for recording the friction. The load is applied by a powerful spring worked by a cam and lever and the limit of the machine is 6000 lbs., total load; careful calibration of the spring showed it to be properly adjusted.

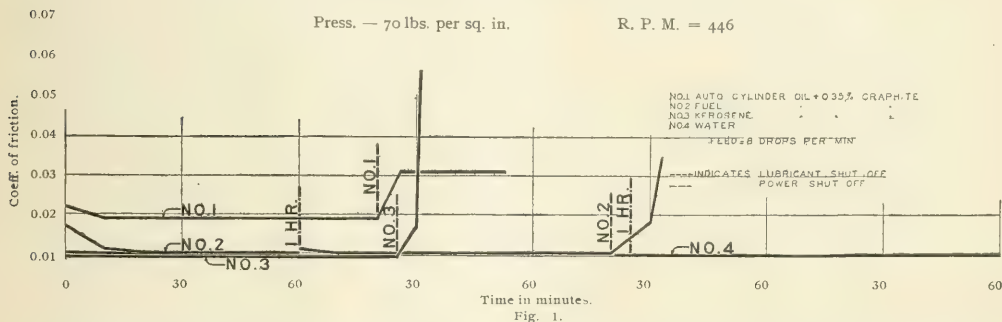
In projected area the bearing in use is approximately 8 sq. in.; the journal is about 3 in. in circumference nearly equal to 1 foot in linear extension. A cast-iron frame babbitted and milled down to a true surface was used for the most part in this work. Even after careful milling some continued frictional work was necessary on the babbitt surface to bring it to the proper conditions of constant results. The hard form of babbitt mentioned above gave satisfactory results, and there was little difficulty in keeping the surfaces in suitable condition after they were once obtained. For measuring temperatures a thermometer was inserted in a hole in the bearing which extended close to the journal. Tests made at steam temperature, 210° Fahr., were carried on with the aid of a hollow cast-iron babbitted bearing, with steam attachments by which it was found that the desired temperature could readily be maintained. The lubricant is run in from a sight-feed cup through a small hole close to one side of the bearing with careful regulation of the flow for proper adjustment of the oil feed. For delivery of the lubricant over the entire face of the bearing two channels or grooves are run diagonally across the babbitt face from the inlet hole which gives equal and even distribution; these channels must be carefully gauged for an even flow, otherwise dry spots or streaks appear on the journal accompanied by a sudden greatly increased friction



indicated on the friction bar. This detail of operation requires careful and constant attention, for on it depends the continuous regularity of the friction curve. In this respect this method of observation is extremely sensitive, and is one of the important elements in frictional tests. Partial exposure of the journal enables the operator to observe the formation

this machine may be readily ascertained on any other equally efficient machine. In duplicate tests made with the same bearing and under the same conditions, the results were closely concordant. At the outset it should be clearly understood that these tests must be performed with a scientific accuracy of exact quantitative observations, with close supervision of

### CURVES OF FRICTION WITH VARYING VISCOSITY OF LUBRICANT

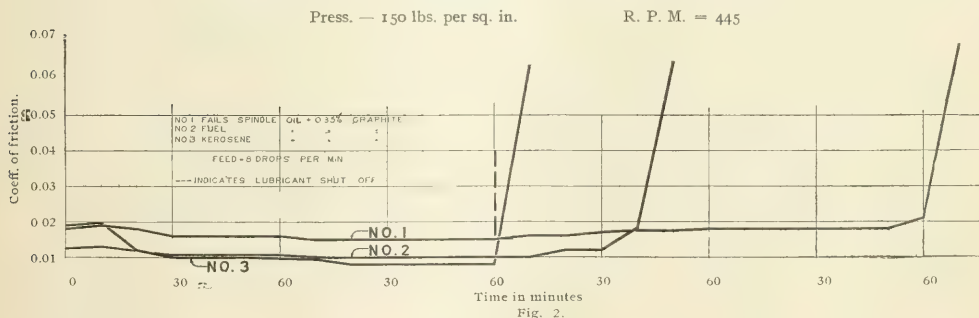


of the film, its comparative thickness and any irregularity due to an imperfect condition of the journal or bearing, or improper lubrication.

Accurate testing of the mechanical efficiency of oils with the precise quantitative observations possible on the Carpenter machine, including the various classes of lubricants under consideration in this

all details; the work then becomes the regular routine of any scientific investigation which involves long series of observations; after it is ascertained by preliminary trial what conditions are necessary in testing any given oil? of course for commercial benefit these conditions should be as close as is practicable to the factory conditions of use.

### CURVES OF FRICTION WITH VARYING VISCOSITY OF LUBRICANT



paper represented an extensive field of labor, especially since there are no general standards of comparison under any conditions of operation. Such constants must of necessity be based on arbitrary data; nevertheless if they are accurately determined on a standard machine, with the conditions of the journal and bearing selected—the load and speed—the constants on

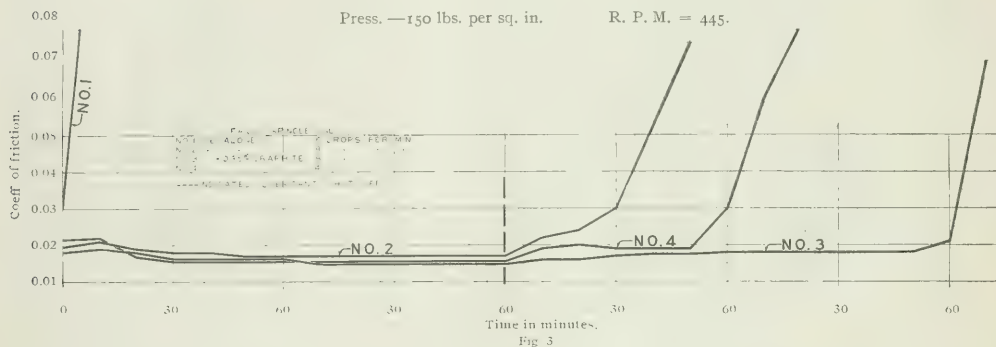
The results to be described on the use of water, kerosene, and fuel oil, as vehicles of graphite present novel and interesting features. Under certain conditions as mentioned above in steam cylinders, it is well known to engineers that water alone serves as a lubricating film. But since on journals it serves no purpose whatever, the lubricating qualities of

aqueous suspended graphite must be due wholly to the graphite. The same is true of kerosene, which alone is practically devoid of lubricating quality, and likewise of fuel oils.

For the purpose of testing the effects of varying viscosity in lubricants, and at the same time the lubricating quality of deflocculated graphite, tests

by a dotted line in the figure, and it appears that there was no change whatever in the direction of the curve by stopping and starting. Curve No. 3, representing the observations on the coefficient for kerosene oil with graphite, is also a straight line, showing a very slightly lower coefficient than water. The coefficient curve for the fuel oil and graphite

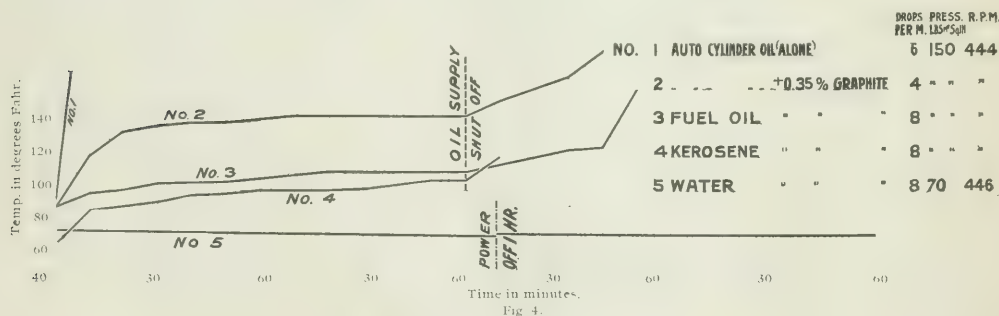
### CURVES OF FRICTION OIL AND OILDAG—VARYING FEEDS



were made with water, kerosene oil, a fuel oil, and an auto cylinder oil each carrying 0.35 per cent. graphite. The results obtained in these tests are shown by the curves in Fig. 1, in which the speed, r. p. m., is maintained at 446, and the load at 70 lbs. per sq. in. The observations of frictional load and temperature were made at intervals of ten minutes each, and on that basis a curve is drawn for each

is also practically a straight line, and with an endurance test extending  $1\frac{1}{2}$  hours after the oil supply was shut off; here the frictional coefficient is slightly higher than that either of water or kerosene. A similar regularity appears in the curve of the auto cylinder oil with graphite, but it is to be noted that the frictional coefficient is very materially higher than those of the other lubricators shown in the figure,

### TEMPERATURE CURVES FOR LUBRICANTS OF VARYING VISCOSITY WITH AND WITHOUT GRAPHITE



of the lubricators tested; in the figure the time is given in half-hour limits and the coefficient of friction in hundredths of a unit. It will be observed that the curve for water and graphite is practically a straight line with scarcely any variation for the four hours shown on the curve; this test continued altogether for 15 hours with a precisely similar result. There were several stops which are indicated

which may be considered as a measure of comparative greater internal viscosity of the auto oil; this oil showed a much longer endurance test than appears in this figure.

The effect of varying viscosity in lubricants and the lubricating quality of the graphite under practically the same speed, 445 r. p. m., but with a load of 150 lbs. per sq. in. using kerosene, a fuel oil and a

spindle oil, with the same proportion of graphite, and the same oil supply is shown in Fig. 2. Kerosene here shows a very slight irregularity in its coefficient, which differs only slightly from that in the preceding figure. Here again the greater internal viscosity of fuel oil is shown by the increased friction which appears in this curve. No doubt the fuel oil possesses the quality of oiliness in a very slight degree which enables it in the beginning of the test to take a lower coefficient than kerosene, which maintains for a few minutes a considerably higher coefficient until the continuous film of graphite has been formed and reduced the coefficient to its normal condition. It is evident that the fuel oil also possesses a certain oiliness which enables it to begin the test with a coefficient that changes only slightly during the entire period, including also an endurance test extending through two hours before

cating quality of the oil is also shown in curves Nos. 3 and 4, curve No. 3 representing a feed of 8 drops per min., and curve No. 4 a feed of 4 drops per min. The diminished coefficient in curve No. 4 as compared with curve No. 4 represents the lubricating effect of graphite, and this effect is still further shown by the increased endurance test in curve No. 4; it will also be observed that besides diminishing friction, curve No. 4 is based on an oil supply due to the graphite, one-half that of curve No. 2 of the oil alone.

In Fig. 4 curves are shown which represent the temperatures recorded in tests of friction presented in Figs. 1 and 2. As in the previous figures the load is given as 150 lbs. per sq. in. for the auto oil, fuel oil and kerosene and 70 lbs. per sq. in. for water. The speed was 444 r. p. m. in all but the test with water where the load was 446 r. p. m.

### AMERICAN CYLINDER OIL WITH AND WITHOUT GRAPHITE

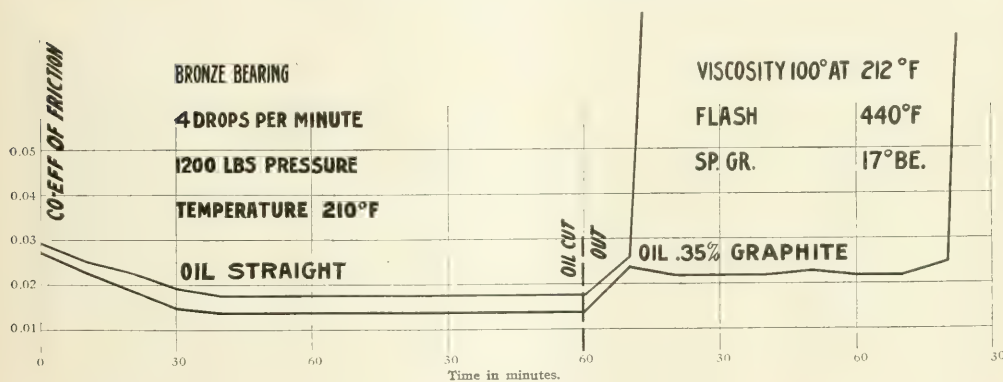


Fig. 5.

the oil breaks and with only a slightly increased coefficient of friction after the oil supply was shut off. Another feature worthy of note is the comparative endurance of the three oils. While kerosene under a bearing load of 150 lbs. per sq. in. maintains an extremely low coefficient, the fact that it breaks immediately when the oil supply is shut off indicates that it has not the power to form a coherent graphite film, which is possessed to some extent by the fuel oil and in a marked degree by the spindle oil.

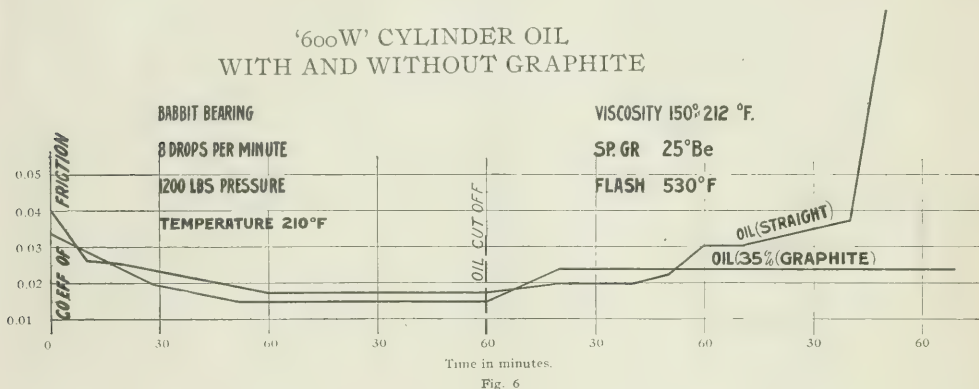
Fig. 3, load 150 lbs. per sq. in., r. p. m. 445, gives the effect on a spindle oil of a variable feed. In one test on the oil alone the oil supply was regulated with the object of breaking the oil at the beginning of the test and also its behavior under an oil supply that enabled it to perform its functions as a lubricant. The effect of graphite on the lubri-

In the test of the auto oil alone there was an immediate rise in temperature corresponding to the breaking point of the oil, which is shown in the friction test. It is interesting to compare this temperature with that of curve No. 2, auto oil and 0.35 per cent. graphite, in which the temperature rises within twenty minutes to a definite point and then continues in a nearly straight line with little variation to the point where the oil supply was shut off at the end of two hours. The curve No. 3, representing the temperatures of fuel oil and graphite, also shows a very slight variation after 30 min., when the stable conditions of lubrications were established. A difference in temperatures of approximately 25° is shown between the curves of the auto and fuel oils which must represent the larger escape of energy in the form of heat from the bearing due to the greater internal resistance of the auto oil. The tempera-



tures of kerosene with graphite as shown in curve No. 4, are approximately  $10^{\circ}$  lower than those in the fuel oil curve, due to the still smaller internal resistance of kerosene. Bearing in mind the small difference between the specific gravity of the fuel oil, approximately  $35^{\circ}$  Bé., and that of kerosene, approximately  $45^{\circ}$  Bé., the difference in temperatures

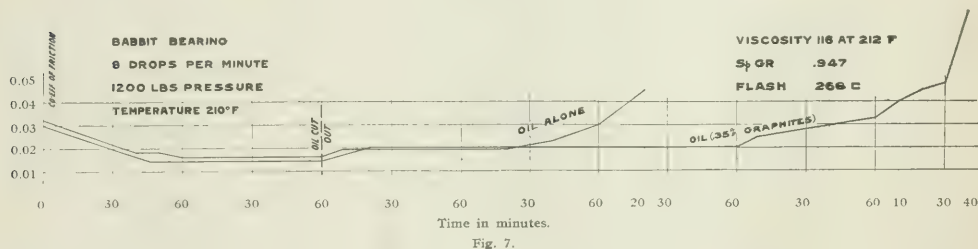
aminated in this work, considerable attention has been given to the behavior of heavy engine and cylinder oils, both straight hydrocarbon oils and compounded oils. An especial form of bearing was constructed consisting of a cast-iron frame with a hollow chamber for introducing steam and a babbitted face using the exceptionally hard babbitt previously described.



of these two curves is a good example of the accuracy in observation possible in these tests. Perhaps the most striking feature in this figure is the curve presenting the temperatures for water and graphite; here as in the curve of friction for water, this curve is shown for only four hours, but the test actually extended through a period of 15 hrs., during which time there were several stops, in which, as shown in this figure, the temperature at the start was the same as that at the time of interruption. It will be observed that this figure shows an extremely

In some of these tests a bronze bearing similarly constructed, only maintaining the bronze face, was employed. But in general, it was observed that the results were less satisfactory not only in testing the heavy oils, but in the other classes of oils examined with the bronze than with the babbitted bearings. Hard babbitt seems to possess certain peculiar qualities adapted to the various details and variations in speeds, loads, and temperatures, which are not found in the same degree in the bronze alloys. To show the results obtained in testing cylinder

### GALENA CYLINDER OIL WITH AND WITHOUT GRAPHITE



low temperature,  $65^{\circ}$ , practically the same as the room temperature, which it never exceeded by more than  $5^{\circ}$ , and that it is essentially a straight line from start to finish. In this use of water as a vehicle for the graphite there is nothing to interfere with the best work that the graphite is capable of performing.

Among the various classes of lubricating oil ex-

oils, figures are here presented on three commercial products, the American cylinder oil, Galena cylinder oil, and "600 W" cylinder oil. Tests were also made on the influence of graphite on these oils with reference to the frictional coefficient and endurance of the oils. The physical constants of the oils are also given for comparison, especially of specific gravity

and viscosity. A general procedure of the tests included a continuous run for two hours, at which time the supply of oil was shut off.

In Fig. 5 of the American cylinder oil, which is a straight hydrocarbon oil, the data of the tests includes the use of a bronze bearing, a supply of lubricant at the rate of four drops per minute, a total pressure of 1200 lbs. and a speed of 245 revolutions per minute. The curve of the oil straight begins at a somewhat higher coefficient than it maintained after the first half hour when normal conditions are established, and it then proceeds in a straight line with no variation to the point where the feed is stopped; the endurance run of this oil is doubtless considerably shorter than it would have been in the use of babbitt bearings; in fact, this was demonstrated in another test in which babbitt was used. With graphite the oil follows closely the direction of the other curve, but with a very considerable diminution in the coefficient of friction, it further appears in the endurance test that the graphite carries the load with slightly increased friction for a period of 1 hour and 20 minutes, which would have doubtless been considerably prolonged if babbitt had been used.

Fig. 6 presents results obtained in tests of the "600 W" cylinder oil with and without graphite. A comparison of physical constants with those in Fig. 5 shows a materially lower specific gravity and somewhat higher viscosity. In these tests the same total pressure, 1200 lbs., and the same speed, 245 revolutions per minute, were used, but the oil feed was double that in the preceding tests and the babbitt bearing was employed. On account of the greater viscosity the straight oil showed at the beginning a considerably higher coefficient and the tests continued one hour before the oil had reached normal conditions, which it maintained until the feed was stopped and which it doubtless would have continued indefinitely. After the oil was shut off lubrication was maintained with some slight irregularity and increased friction during 1 hour and 40 minutes, the point at which it broke. Similar conditions are observed in the curve which expresses the variation in the coefficient of friction of this oil with 0.35 per cent. graphite; it begins the test with a somewhat lower friction and reaches normal conditions sooner than the straight oil, and continues in a straight line to the point where the supply is stopped, and then still continues in a straight line with somewhat increased friction. The endurance curve would doubtless have continued for a considerably longer time but the power was shut off at the point where the curve terminates. A marked influence of graphite on the behavior of this oil is plainly apparent in a comparison of these curves.

In applying tests to the Galena cylinder oil with

and without graphite, the same feed, load and pressure were used as with the preceding oil and the tests were made on a babbitt bearing. In viscosity this oil is somewhat less than the preceding oil, the specific gravity somewhat higher. Both curves begin with a slightly lower coefficient, 0.03, and this difference is maintained until the oil is shut off and for  $1\frac{1}{2}$  hours on the endurance test. To reach normal conditions the straight oil ran for one hour, the oil with graphite 45 minutes. After the feed was stopped, the curves proceed regularly with slightly increased friction, the oil alone practically breaking in  $1\frac{1}{2}$  hours, the oil with graphite proceeding with perfect regularity for three hours, changing slightly during the next hour and breaking at the end of  $4\frac{1}{2}$  hours. The tests represented on Figs. 5, 6 and 7 are not intended to present a comparative efficiency of these particular oils but to demonstrate the application of this method of testing and also to compare the effects of deflocculated graphite.

The results presented in this paper with reference to the uses of graphite as a solid lubricator indicate that in the deflocculated form it can readily be applied with great economic efficiency in all forms of mechanical work. One of its most characteristic effects is that of a surface evener by forming a veneer equalizing the metallic depressions and projections on the surfaces of journal and bearing, and endowed with a certain freedom of motion under pressure, it affords the most perfect lubrication. In automobile lubrication the great efficiency of graphite in increasing engine power, in controlling temperatures, and wear and tear of bearings has been brought out in a series of tests conducted by the Automobile Club of America. In connection with the reduction in friction of lubricating oils by graphite the extremely small proportion necessary is worthy of note; the proportion used in this work is equivalent to a cubic inch of graphite in 3 gallons of oil. The curve of temperature for Aquadag, an increase but slightly above that of the surrounding atmosphere, demonstrates an important economic quality of controlling temperatures in factory lubrication, and thereby avoiding the danger of highly heated bearings, which are frequently the cause of fires.

In the observations described in this paper, and, in fact, in all the work that has been done in this field, there is not a more impressive example of the efficiency of graphite in lubrication than that presented in the curves of friction and temperature of water and graphite; for water serving merely as a vehicle and completely devoid of lubricating quality, the graphite is permitted to perform its work without aid and with no limiting conditions.

## STUDIES ON THE CARBENES.

By KENNETH GERARD MACKENZIE.

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In 1905, Richardson and Forrest<sup>1</sup> called attention to the use of carbon tetrachlorid as a solvent for differentiating bitumens. They showed that the amount of bitumen soluble in carbon disulphid, but insoluble in carbon tetrachlorid, furnished an indication of the amount of weathering to which natural asphalts had been subjected; and also revealed careless refining of the residual pitches obtained from California and Texas petroleum, having an asphaltic base. Mr. Richardson, in his "The Modern Asphalt Pavement,"<sup>2</sup> applied the name of "Carbenes" to this class of substances. Recently, Kirschbraun<sup>3</sup> has carried on extensive experiments upon the effect of overheating on the carbene content of Bermudez asphalt and cement. His "results \* \* \* confirm the correctness of Clifford Richardson's conclusion that carbenes are a result of overheating."

Again on the Pacific Coast, tetrachlorid has largely been used by municipal authorities and by producers as a means of controlling the character of the residual pitch, which is produced there to such a large extent for paving purposes.

Certain discrepancies having been noted between the results of determinations of carbenes in the same samples, made in the New York Testing Laboratory and in another laboratory on the Pacific Coast, an investigation was undertaken by the writer at the suggestion of Mr. Richardson with the object of discovering the cause.

The first possible explanation was a possible difference in the purity of tetrachlorid used. All tetrachlorid in use in this laboratory is distilled with a Young 18-column dephlegmator, discarding all boiling below 76°, thus removing any traces of carbon disulphid which may be present. To determine the effect of CS<sub>2</sub> impurities upon the amount of carbenes, samples of Durango and Texas pitch were examined.

TABLE I.—CARBENES IN TEXAS PITCH

	Per cent
Pure tetrachlorid .....	9.3
Tetrachlorid 2½ per cent. CS <sub>2</sub> .....	9.5-9.5

TABLE II.—CARBENES IN DURANGO No. 107979.

	Per cent.
Pure tetrachlorid .....	3.7
Tetrachlorid 5 per cent. CS <sub>2</sub> .....	3.3
Tetrachlorid water saturated .....	3.6

The amount of disulphid would never exceed 5 per cent., and the effect of a less amount is negligible. Likewise water has no effect on the solvent power, for tetrachlorid dried over sodium will absorb less than 1 part in 5000.

Mr. Richardson has already called attention<sup>1</sup> to the fact that the carbene precipitate is in a very finely divided condition, and that, after dissolving in tetrachlorid, the solution must stand over night to ensure coagulation. It at once suggested itself that we might be dealing with a colloid which gradually changed to an insoluble precipitate, the carbenes, when solution first took place, being nearly all in the form of a colloidal solution, which on standing were precipitated. If this were so, with sufficient standing and several filtrations we should be able to obtain the true carbene value.

TABLE III.—CARBENES IN DURANGO No. 107979.

	Per cent.
Dissolved, stood over night and filtered .....	6.5
Refiltered next day, obtained additional .....	4.2
Stood over two days, refiltered, additional .....	2.2
Stood over one day, refiltered, additional .....	0.3
Total .....	13.2

We have thus evidently removed all the carbenes since a final standing of 48 hours gave only 0.3 per cent.

TABLE IV.—CARBENES IN DURANGO No. 107979.

	Per cent.
Air blown one hour, stood over night .....	5.9
Refiltered after standing over night, with very tight asbestos pad, additional .....	6.9
Total .....	12.8
Dissolved, stood over night and filtered .....	3.7
Refiltered after standing one and one-half weeks, additional ..	10.2
Total .....	13.9
Dissolved in tetrachlorid with 5 per cent. CS <sub>2</sub> stood over night and filtered .....	3.3
Refiltered after 1½ weeks, additional .....	10.9
Total .....	14.2

We see that, after long standing, we obtain thirteen to fourteen per cent. carbenes, though, with a very tight filter, two days' standing gives us almost as large an amount. One other trial gave:

TABLE V.—CARBENES IN DURANGO No. 107979.

	Per cent.
Dissolved, etc., as usual .....	3.5
Refiltered after four days, additional .....	10.1
Total .....	13.6

It would thus seem that to obtain the true amount of carbenes, it is necessary to allow the solution to stand at least four days. This should give sufficient time for the complete coagulation and precipitation of these hydrocarbons.

At this time, our attention was called<sup>2</sup> to the possibility of the amount of carbenes being effected by exposure to light. Accordingly samples were taken, in octoplicate, of Gilsonite selects, Texas pitch and Durango No. 107979. They were treated as shown below.

SOLUBILITIES IN CS<sub>2</sub>.

	Per cent.
Gilsonite .....	99.8
Texas pitch .....	96.1
Durango .....	99.4

<sup>1</sup> "Modern Asphalt Pavement," 2nd edition, p. 546.<sup>2</sup> By D. B. W. Alexander. See also *J. Am. Chem. Soc.*, **31**, 1052.<sup>3</sup> *J. Soc. Chem. Ind.*, **24**, 7.<sup>4</sup> First edition, p. 120.<sup>5</sup> *Minneapolis Engineering*, **35**, 349.



TABLE VI.—GILSONITE.

	A.	A'.	B.	B'.	C.	C'.	D.	D'.
FIRST DAY:								
Dissolved in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	3.30 P.M.	3.30	3.30	3.30	3.30	3.30	3.30	3.30
SECOND DAY:								
Filtered in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	8.30 A.M.	8.30	8.30	8.30	8.30	8.30	8.30	8.30
Transferred to	..	..	Light	..	..	..	Dark	..
Time.....	..	..	3.30 P.M.	..	..	..	11.30 A.M.	..
THIRD DAY:								
Filtered in...	Dark	..	Light	..	Light	..	Dark	..
Time.....	11.00 A.M.	..	8.00 A.M.	..	8.00 A.M.	..	11.00 A.M.	..

TABLE VII.—TEXAS PITCH.

	A.	A'.	B.	B'.	C.	C'.	D.	D'.
FIRST DAY:								
Dissolved in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	3.30 P.M.	3.30	3.30	3.30	3.30	3.30	3.30	3.30
SECOND DAY:								
Filtered in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	8.30 A.M.	8.30	8.30	8.30	8.30	8.30	8.30	8.30
Transferred to	..	..	Light	Light	..	..	Dark	Dark
Time.....	..	..	4.30	3.30 P.M.	..	..	5.00	5.00 P.M.
THIRD DAY:								
Filtered in...	Dark	Dark	Light	Light	Light	Light	Dark	Dark
Time.....	8.30	2.00	8.00	1.00	8.00	1.00	8.30	2.00
Transferred to	..	..	Light	Dark	..	..	Dark	Light
Time.....	..	4.00	4.00	..	..	4.00	4.00	..
FOURTH DAY:								
Filtered in...	Dark	Light	Dark	Light	Light	Dark	Light	Dark
Time.....	7.30	7.30	10.00	7.30	7.30	10.00	10.30	10.30

TABLE VIII.—"D" GRADE.

	A.	A'.	B.	B'.	C.	C'.	D.	D'.
FIRST DAY:								
Dissolved in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
SECOND DAY:								
Filtered in...	Dark	Dark	Dark	Dark	Light	Light	Light	Light
Time.....	8.30 <sup>1</sup>	8.30	8.30	8.30	8.30	8.30	8.30	8.30
Transferred to	..	..	Light	Light	..	..	Dark	Dark
Time.....	..	..	3.30	3.30	..	..	11.30	11.30
THIRD DAY:								
Filtered in...	..	Dark	Light	Light	Light	Light	Dark	Dark
Time.....	..	8.30	8.00	1.00	8.00	1.00	8.30	2.00
Transferred to	..	..	Dark	..	..	Dark	Light	..
Time.....	..	..	4.00	..	..	4.00	4.00	..
FOURTH DAY:								
Filtered in...	Dark	Dark	Dark	Light	Light	Dark	Light	Dark
Time.....	7.30	7.30	7.30	7.30	7.30	7.30	7.30	7.30

TABLE IX.—CARBENES OBTAINED.

	SECOND DAY.	THIRD DAY.	FOURTH DAY.
GILSONITE:			
A.....	0.0	0.07	...
A'.....	0.0	...	...
B.....	0.0	0.07	...
B'.....	0.04	...	...
C.....	0.07	0.15	...
C'.....	0.00	...	...
D.....	0.07	0.13	...
D'.....	0.0	...	...
Texas:			
A.....	7.3	0.2	0.1
A'.....	7.4	0.2	0.9
B.....	7.3	1.5	3.1
B'.....	7.2	2.6	1.7
C.....	11.4	3.2	0.6
C'.....	11.2	2.8	0.3
D.....	12.2	2.0	0.6
D'.....	11.5	2.4	0.1
DURANGO:			
A.....	4.8	...	0.4
A'.....	5.1	0.2	0.1
B.....	5.0	1.9	4.4
B'.....	5.0	3.0	2.0
C.....	9.0	3.2	0.5
C'.....	9.2	2.8	0.2
D.....	8.5	0.2	0.5
D'.....	8.4	0.3	0.1

<sup>1</sup> Filtering and washing two days.

The samples of Gilsonite showed practically no carbenes, and require no comment. The Texas pitch, however, gives some interesting results. "A" was carried out entirely in the dark, and showed that all the carbenes were removed by the first filtration. "C" manipulated entirely in the light gave 4 per cent. more carbenes on the initial filtration, and a further increase of 3 per cent. on the second filtration. A third filtration gave, however, practically no more. Where samples first stood in the light and then in the dark, it should be noticed that they were filtered in the light, and, after the filtration was complete, were transferred to the dark. But, after passing through the Gooch, the solution was exposed a drop at a time to light, and the filtrate remained in the light until all was filtered. In Table VII, the "time filtered" shows the time filtration commenced, "time transferred," when it was complete. Thus we see that B standing in the dark gave 7.3 per cent. Further standing in the light gave 1.5 per cent., and further standing in the dark 3.1 per cent. This very contradictory result is explained when it is noticed that before bringing back into the dark, it was light exposed from 8:30-4:30, while the filtration was in progress. This may be criticized as an unwise method of procedure, but on the other hand, where different fineness of filters required different lengths of time for filtration, the amount of carbenes is proportional to the length of exposure during filtration, and tends to all the more firmly establish the fact that the amount of carbenes is very largely increased by the action of light.

Turning now to the Durango, we find a further confirmation. "A" carried on entirely in the dark gave at first 5.1 per cent., and practically no more on further standing. "C," light-exposed, gave at first 4 per cent. more than "A," a second filtration an increase of 3.2 per cent., while a third filtration gave only an additional half per cent. The total was 12.7 per cent. in close agreement with figures obtained before on the same sample. The figures outside of the initial amounts are strikingly similar to the Texas pitch. Likewise B, as above, gave an exceptionally large per cent. on the final filtration. Standing and filtering in the dark, it had then stood in the light, but since there was no agitation, carbenes were precipitated only in the outer layers of the solution. On filtering in the light, the whole solution was thoroughly light-exposed after filtration, and, though it stood finally in the dark, the carbenes had already been precipitated.

"G" Grade flux, Extra Heavy flux and a blown oil, which under ordinary conditions had no carbenes, were dissolved in tetrachlorid, and the solutions exposed to sunlight for three weeks.

Solutions of Bermudez refined asphalt and Trinidad refined asphalt were allowed to stand 19 days.

TABLE X.—CARBENES FROM FLUXES ON THREE WEEKS' LIGHT EXPOSURE.

	Per cent.
"G" grade.....	7.6
Extra heavy.....	0.3
Blown oil.....	0.9

TABLE XI.—CARBENES FROM BERMUDEZ AND TRINIDAD REFINED ASPHALTS.

BERMUDEZ		Per cent.
Standing in the dark.....		0.0
Standing in north light.....		1.3
Standing in sunlight.....		1.3
TRINIDAD.		Per cent.
Standing in the dark.....		3.0
Standing in north light.....		8.2
Standing in sunlight.....		10.7

It is seen, therefore, that the class of substances usually determined as carbenes consists of two kinds of hydrocarbons: those which are precipitated in a tetrachlorid solution, in the dark, completely on standing 12 hours; and those which are precipitated from the tetrachlorid solution by the action of light and are usually *not* completely precipitated by standing 12 hours. To the first class of substances we have given the name pure carbenes since they are evidently the true constituent of the bitumen soluble in carbon bisulphid and insoluble in carbon tetrachlorid. To the second class the name "pseudo carbenes" needs no comment. The total carbenes are the sum of these two.

The work of Kirschbraun was then repeated, determining the carbenes in the pure and pseudo forms. In each case, about 700 g. of bitumen were heated in a round-bottomed flask of twice that capacity on an air bath, with air agitation. The carbene determinations were made running parallel samples in the dark and in north light with a 12-hour stand. The pure carbenes is the amount insoluble in tetrachlorid in the dark less the amount insoluble in carbon bisulphid. The pseudo-carbenes is the difference between the  $\text{CCl}_4$  insolubles in light and dark.

TABLE XII.—DUPLICATION OF EXPERIMENTS BY KIRSCHBRAUN. BERMUDEZ ASPHALT CEMENT 100 PARTS, BERMUDEZ R. A. 26 PARTS, K. CO. PARAF. FLUX.

	Original.	Heated 2 hrs. at		Heated 2 hrs. longer at	
		300° F.	400° F.	500° F.	700° F.
Bitumen.....	97.9	97.9	97.8	98.0	97.9
Min mat.....	1.2	1.3	1.2	1.2	1.5
Organic non-bitumen.	0.9	0.8	1.0	0.9	0.6
Malthenes 88°					
Naph. in asphalt.....	75.1	75.0	70.0	65.1	53.8
Malthenes 88°					
Naph. in bitumen.....	76.7	76.6	71.2	66.5	54.9
Pure carbenes.....	0.0	0.0	0.0	0.0	0.0
Pseudo-carbenes.....	0.0	0.0	0.0	0.0	0.7
Total carbenes.....	0.0	0.0	0.0	0.0	10.7
Penetrometer.....	119	102	68	35	7
Fixed carbon.....	13.0	12.7	12.9	14.5	19.6

These results agree in the main with those of Kirschbraun. A larger amount of carbenes is obtained in the final stage, but conditions could not be exactly similar, and we cannot be sure, since he gave no figures, that the fluxes used were evenly approximately similar. It is especially worthy of note that

the carbenes from overheated Bermudez asphalt cement come down almost completely in the dark, and that the light has very little additional precipitating action. The results on Bermudez refined asphalt follow:

TABLE XIII.—BERMUDEZ REFINED ASPHALT. DUPLICATION OF EXPERIMENTS BY KIRSCHBRAUN.

	Original.	Heated to 500° F. 2 hrs.	Heated to 500° F. 4 hrs.	Heated to 500° F. 6 hrs.	Heated to 700° F. 2 hrs.
		for 2 hrs.	for 4 hrs.	for 6 hrs.	longer.
Bitumen.....	97.5	97.7	97.3	97.5	97.4
Min. mat.....	1.5	1.5	1.6	1.5	1.9
Organic non-bitumen.....	1.0	0.8	1.1	1.0	0.7
Malthenes 88°					
Naph. in asphalt.....	73.9	68.8	63.2	60.1	57.3
Malthenes 88°					
Naph. in bitumen.....	75.9	70.2	64.9	61.4	58.8
Pure carbenes.....	0.0	0.0	0.0	0.0	0.0
Pseudo-carbenes.....	0.0	0.0	0.0	0.0	0.0
Total carbenes.....	0.0	0.0	0.0	0.0	0.0
Penetrometer.....	16	6	4	2	5
Fixed carbon.....	15.2	16.3	17.8	19.2	25.6

No carbenes were found, while Kirschbraun in his final heating obtained 25.8 per cent. There seems to be no explanation available for this discrepancy. Kirschbraun worked with a smaller amount, but even if he had obtained local overheating, it would in all probability have only increased the free carbon. The absence of carbenes even from overheated Bermudez asphalt would be expected.

In order to further examine the effect of overheating upon the pure and pseudo-carbenes, a sample of Durango, California, asphalt was treated as above.

TABLE XIV.—EFFECT OF HEATING UPON THE CARBENE CONTENT OF DURANGO ASPHALT.

	Original.	Heated to 400° F. 2 hrs.	Heated to 500° F. 2 hrs. longer.	Heated to 600° F. 2 hrs. longer.	Heated to 700° F. 2 hrs. longer.
Bitumen.....	99.7	99.6	99.7	99.8	78.8
Min. Mat.....	0.2	0.1	0.1	0.1	0.1
Organic non-bitumen.....	0.1	0.3	0.2	0.1	22.1
Malthenes 88° in asphalt.....	79.2	77.0	73.2	64.8	46.2
Malthenes 88° in bitumen.....	79.4	77.3	73.4	64.9	58.6
Pure carbenes.....	2.3	1.7	2.2	4.0	15.0
Pseudo-carbenes.....	3.2	4.2	3.8	5.8	1.5
Total carbenes.....	5.5	5.9	6.0	9.8	16.5
Penetrometer.....	87	54	28	9	too hard.
Fixed carbon.....	14.7	15.5	16.9	20.2	33.2

Except in the final heating, the pseudo-carbenes were slightly larger than the pure. The fixed carbon and 88° naphtha insoluble increased gradually, but the bitumen remained constant. When heated to 700° F. 22 per cent. of free carbon was formed and the carbenes, 16.5 per cent., were almost entirely precipitated in the dark.

In order to investigate further the nature of the carbenes, 60 g. of a different Durango were dissolved in the dark in 6 l. of tetrachlorid. It was allowed to stand over night and filtered in the dark.

Yield, about 1.5 g., equivalent to 2.5 per cent. The Durango contained 0.4 per cent. mineral matter and 1.0 per cent. total insoluble in carbon bisulphid.

Thus pure carbenes were 1.5 per cent.

The solution was then placed outside (June 14, 1909) and allowed to remain 22 days. There was, during this period, continuously clear weather, part of it extremely hot. The solution was then filtered.

Yield, pseudo-carbenes 8.23 g. equivalent to 13.7 per cent.

It may be noted here that, on opening the container after the light exposure, the odor of hydrochloric acid was plainly perceptible.

The pure carbenes (combined, of course, with the disulphid insoluble) did not melt even at a red heat. They contained nitrogen and sulphur.

The pseudo-carbenes decomposed with effervescence on heating above 300°. They also contained nitrogen and sulphur.

They had the following properties:

	Per cent.
Soluble 88° naphtha.....	3.3
Soluble hot chloroform.....	98.5

They seemed to be sparingly soluble in disulphid, for though the insoluble(?) residue was washed continually, the washings were always colored. The results from one trial will show this.

	Per cent.
Taken 0.5000 gram	
Dissolved in 100 cc., washed with 125 cc., dissolved	16
Washed further with 200 cc., dissolved further.....	6.6
Washed further with 200 cc., dissolved further.....	4.7

This would at once suggest that those compounds called carbenes were not present as such in the original bitumen, for, as stated above, all but 1 per cent. of the Durango was very readily soluble in a small amount of bisulphid.

This conviction was strengthened when it was found that both the pure and pseudo carbenes contained 3 to 4 per cent. of chlorine.

The original Durango, of course, contained none.

When, in recovering tetrachlorid from bitumen solutions, it is run down to dryness in the retort, hydrochloric acid is evolved. One case gave as much as 96 mg. per liter in the distillate. Thus, evidently, tetrachlorid is decomposed by bitumen when heated with it. It has already been noted that when the container with the tetrachlorid solution after sunlight exposure was opened, the odor of hydrochloric acid was quite evident.

Could it not be that by the action of light as well, hydrochloric acid is formed, which combines with certain unsaturated hydrocarbons and forms precipitates?

In order to find the effect of hydrochloric acid upon the carbene figure, 1 g. of Durango, used to prepare the pure pseudo-carbenes, was dissolved in 100 cc. tetrachlorid and dry HCl passed through for one hour. A duplicate was air-blown for a similar time to check the result. Both were allowed to stand over night.

	Per cent.
Carbenes by HCl.....	21.8
Carbenes by air-blowing.....	4.4

The Durango submitted to high temperatures above was examined in the same way, giving the following amount of carbenes:

	Per cent.
ORIGINAL.....	24.2
After heating up to 600° F.....	38.0
After heating up to 700° F.....	33.9

Hydrochloric acid causes thus a large increase in the amount of carbenes, and the hypothesis already suggested finds confirmation, namely:

*That light acting upon a solution of bitumen in tetrachlorid causes the bitumen to decompose, the tetrachlorid giving hydrochloric acid, which in turn combines with unsaturated hydrocarbons and precipitates them.* But only certain bitumens (namely those which have been more or less overheated) can bring about this phenomenon. Bermudez asphalt is practically unreactive.

We are thus forced to the conclusion that in overheating certain decomposition products are formed, which compounds are capable of reacting with the tetrachlorid; or, that an excess of HCl is naturally generated and by overheating, compounds capable of combining with it are formed.

We have to consider the pure carbenes which also contain chlorin and which are formed *without the aid of light*. With our present knowledge, it is useless to devise any theory to distinguish between these two classes. Much further work is necessary.

Opponents of the carbene determination will apparently find in this new ammunition for their warfare. But, after all, has the carbene lost any of its value? It is to be sure affected by light, but, if conditions are relatively the same, if the solution is allowed to stand over one night, as Mr. Richardson suggests, and if it is kept from direct sunlight, very concordant results may be obtained. What if by long exposure the amount may be increased? The same effect can be obtained by using hydrochloric acid gas, yet we would not think of taking the amount so obtained as the carbene figure. Like many other determinations in bitumen analysis, the carbenes are more or less arbitrary, but they do show, proportionally, when weathering or overheating has taken place, and as Kirschbraun states:<sup>1</sup> "The amount of carbenes allowable in asphalts must as yet be a matter of opinion, until sufficient data are available to determine such limits.

In the meantime, unless it can be conclusively shown from practical results that asphalts high in carbenes make satisfactory pavements, a discrimination against such asphalts is, at present, logical and safe.

NEW YORK TESTING LABORATORY,  
MAURER, N. J.,  
January 14, 1910.

<sup>1</sup> Loc. cit.





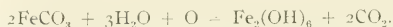
goes on comparable to respiration, but consisting in the oxidation of inorganic compounds. Belonging to this class, some of the thiobacteria possess the unique power in organic creation of breaking up sulphur compounds and assimilating into the cells of their protoplasm pure sulphur, which is subsequently oxidized into sulphuric acid. Leaving aside tempting speculation concerning the mode in which life interacts or is associated with matter, the data at hand seemed to warrant the belief that an important connection existed between bacterial activity and underground corrosion. Whatever produces acid conditions in the soil must contribute in no small manner to the corrosive influences present. That acid compounds are formed in abundance as the result of vital activity is easily demonstrated.

Important recent advances in our knowledge of bacteria are those having reference to the agency of these organisms in the circulation of certain elements in nature. The functions of nitrogen and iron bacteria in this connection have long been known. Definite anaerobic forms also exist which have the power of fixing carbon and sulphur as well as nitrogen from inorganic sources. Owing to the peculiarities in the modes of nutrition and respiration of these bacteria (*vide infra*) they require neither free oxygen nor organic food materials for vital activity.

It is now well known that a whole series of sulphur bacteria exist of the genera thiothrix, chromatium, spirillum and monas, which play important parts both in the circulation and concentration of sulphur in nature. There exist, moreover, in the mud of marshes anaerobic bacteria which decompose cellulose, probably hydrolyzing it first and then splitting the products into carbon dioxide and marsh gas. When calcium sulphate is present, the nascent methane set free by the cellulose bacteria reduces the sulphate with the formation of calcium carbonate, sulphuretted hydrogen and water. This is the explanation of the occurrence of marsh gas and sulphuretted hydrogen in bogs, and such conditions afford favorable media for sulphur bacteria which multiply by oxidizing the sulphuretted hydrogen and storing the sulphur in their own protoplasm. Processes resulting from the bacterial decomposition of vegetable mud only take place at certain depths, and the zone of physiological activity rises and falls with the variations of partial pressures of gases due to the rate of evolution of sulphuretted hydrogen. In the deeper parts of this zone the partially anaerobic bacteria absorb the sulphuretted hydrogen and as this rises and meets atmospheric oxygen other bacteria oxidize it and store up the sulphur; then ascending into planes more highly oxygenated other bacteria further oxidize the sulphur to sulphuric acid, which combines with any calcium carbonate present to form sulphate again. These bacteria, therefore, employ sulphuretted hydrogen

as their source of energy much as higher organisms employ carbohydrates—instead of liberating energy as heat by the combustion of sugars, they do it by oxidizing hydrogen sulphide. One of the anaerobic forms (*Spirillum disulphuricans*) attacks and reduces sulphates, thus undoing the work of sulphur bacteria just as certain denitrifying bacteria reverse the operations of nitro-bacteria. Again, we have sulphur taken into the higher plants as sulphates, built up into proteins, decomposed by putrefactive bacteria, and yielding sulphuretted hydrogen which the sulphur bacteria oxidize, the resulting sulphur is then oxidized to sulphuric acid and again combined with calcium to gypsum, the cycle being thus complete.

The well-known part played by iron bacteria affords an analogy to the circulation and chemical changes just described wrought by the life processes of sulphur bacteria in the widely distributed sulphur compounds in nature. Pools and marshes near iron mines abound in bacteria, some of which belong to the remarkable genera crenothrix, cladothrix and heptothrix and contain ferric oxide in their cell walls. This iron deposit is not merely mechanical, but is due to the physiological activity of the organism which liberates energy by oxidizing ferrous oxide in its protoplasm. The iron must be in certain soluble conditions, and the soluble carbonate of the protoxide seems most favorable. The hydrocarbonate absorbed by the cells is oxidized probably thus:



The ferric hydroxide accumulates in the sheath and gradually passes into the more insoluble ferric oxide. These actions are of great importance in nature, as their continuation results in the enormous deposits of bog iron ore.

The writer has recently been informed of a serious case of corrosion in the West, in which the evidence is apparently conclusive that the damage was due to specific bacteria. During repair work on the foundation structure of a bridge across Lake Hauser, in Montana, the attention of the engineer in charge was attracted to protuberances which occurred with more or less regularity on the steel work of the supporting tubes. The steel construction men designated this "shell rust" and said that it was often seen on steel which had been under water for some time. Mr. Wilton G. Brown, a Montana naturalist, made a careful examination of the protuberances and found that this was not a case of common rust action, but under the center of each individual an irregular pit was eaten into the steel. An inspection of some of the rust material under the microscope soon led to the conviction that some organism had played a part in the destructive corrosion. The phenomena were reported to Professor Beck, of Freiburg, Germany, who suggested that such vigorous action was probably

due to bacteria. Specimens of the rust were then submitted to the eminent bacteriologist, Dr. Shorler of Dresden, who identified *Gallionella ferruginea* in great abundance in the material. The method of attack of this organism is first the elimination of an acid product by which the iron is dissolved, and then each individual forms a pit by eating out the metal. The structural damage was reported to have been enormous for the short period of less than a year that the bridge had been in service.

The foregoing considerations apparently warrant the conclusion that the corrosion of underground iron and steel structures is in part due to bacterial activity:

- (1) Directly, or by the attack of a specific microbe.
- (2) Indirectly, or by creating acid conditions in the soil. Certain bacteria present, owing to peculiar modes of absorption and elimination of sulphur and its compounds convert harmless substances into corrosive acids.

The remedies proposed are:

- (1) Free drainage quickly carrying off the acid solutions formed should arrest or prevent destructive action.
- (2) In localities or situations where drainage is impracticable, slack lime should be packed about the metal, to neutralize acids formed as a result of bacterial activity.

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## VARIATIONS IN CAR PAINTING PRACTICE.

By CARL F. WOODS.

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The past few years have witnessed a wide-spread movement in this country towards the standardization of paint products. Public attention has been called to the prevalence of adulteration and to the practice, particularly in mixed paints, of selling goods of short weight, while certain investigators ably supported by the reputable paint manufacturers have revealed many such frauds and have taken decisive steps toward the education of the consumer and the establishment of definite standards. Important data are being accumulated on the relative value of the various pigments and vehicles, but comparatively little attention is being given to the proper application of the paints themselves. The responsibility for poor results in painting rests both with the painter and the paint manufacturer, for although inferior materials cannot be made to give long life even in the hands of the most skilful painter, it is equally true that good paint improperly applied affords no better results than poor paint. There is no class of painting in which this is more clearly illustrated than in that of car finishing, for this is not a comparatively simple operation like house painting, but on the con-

trary is a complex and highly skilful procedure, requiring expert labor and involving the application of many coatings.

The object of car painting is both for protection and for decoration, although the latter consideration has exerted the greater influence on the modern practice of car finishing. It is possible to preserve the woodwork of a car body just as efficiently by frequent painting with suitable oil paints as by covering it with the ten to fifteen coats of paint and varnish customarily applied. This is well illustrated by the practice of the Interborough Rapid Transit Company of New York, who paint the bodies of the subway cars with a dark red house paint. Not a vestige of ornamentation is used and the cars are not even varnished. This is an extreme case, but the practice has been adopted by an experienced management, and indicates the simple method of car finishing which can be used where the appearance of the car is of no importance. The steam or electric car operated on the surface, however, occupies a prominent position, and the public justly demands that it present a well-kept exterior. The appearance and condition of the cars is frequently considered an indication of the liberality of the management, and as a result many companies have carried this idea to an extent which brings an unnecessary burden on the earning capacity of the system. The cost of painting the same type of car varies on different roads from \$30.00 to \$60.00, and in certain cases an even larger amount, while some roads are forced to repaint their cars every two years, and others with the aid of one coat of varnish each year are able to operate for ten to fifteen years before complete refinishing becomes necessary. It is particularly significant that those cars which have had the most expensive finishing are not of necessity the longest-lived. It is obvious, therefore, that there are certain underlying principles upon which the durability of the finish depends.

Car paints as a rule are mixtures of liquids and solids having widely different chemical and physical properties. Between the priming coat and the final varnish, there are not less than twenty elements intimately in contact, some of which have an affinity for each other, while others may tend to dissociate. This is particularly true of varnishes, for two different brands of equal durability may so react as to materially injure the wearing qualities of either one. While each succeeding treatment has its own specific demands, the entire paint coating must amalgamate and act as a unit to prevent separation of the various films under the physical stresses of service, produced by the expansion and contraction of the car under changes of temperature, and the wrenching and twisting incidental to operation. The importance of selecting the right composition for the successive coats is self-evident, but it is equally essential to employ a method



of finishing which will take into consideration the specific demands which are imposed upon each coat.

There are four fundamental operations in car painting which must be performed to obtain the proper finish and the desired durability:

*First*, the pores of the wood must be thoroughly saturated to prevent the absorption of succeeding coats and to form a cementing bond between the wood and the paint films.

*Second*, the natural inequalities of the surface must be corrected and a smooth, hard foundation prepared for the application of the succeeding color and varnish coats.

*Third*, the required color must be applied in a smooth, homogeneous film which is sufficiently thick to cover the underlying coats and which at the same time possesses proper elasticity.

*Fourth*, the color coat must be covered with a film of varnish, both to protect the underlying paints from the effect of the weather and to obtain the glossy, smooth finish desired. It is necessary that this final coat be hard enough to withstand the abrasive action of sand and dirt and the general deteriorating effects of sun, wind and weather, but at the same time possess the maximum amount of elasticity.

Three distinct processes for car finishing are in use, each of which, if properly applied, produces satisfactory results, but obtains the requisite qualities by essentially different methods. These three systems may be called the "Lead and Oil," the "Surfacer" and the "Color and Varnish" Processes. Other methods of finishing are employed but all of them are abbreviations or combinations of the three main types.

The "Lead and Oil" Process is the oldest system in use, and requires the application of the greatest number of coats and the expenditure of the most labor. This process consists in thoroughly saturating the wood with a thin paint of white lead and linseed oil, followed after proper drying by thicker coats of the same paint until the woodwork is properly "primed and filled." On the foundation so prepared, several coats (usually three) of a special paint known as "rough stuff" are applied. This consists essentially of a mineral silicate of moderate fineness mixed with white lead and ground in varnish. Such a paint dries quickly and can be brought by rubbing with blocks of pumice to a smooth, slate-like finish, which affords an admirable surface for the body color. Car colors, often known as coach colors, form a special class of paints and consist of a suitable pigment ground to the last degree of fineness in "Grinding Japan," which is really a special varnish generally made of high-grade shellac, and loaded nearly to the point of saturation with lead and manganese driers. The paint so prepared thinned for application with a suitable amount of turpentine dries readily and affords a smooth homogeneous color.

After a sufficient amount of color has been applied, the entire surface is given several coats of varnish, allowing each to dry thoroughly before adding the next. Two different types of varnish are sometimes employed on the same car: the first a "Rubbing Varnish," which contains from 6 to 12 gallons of linseed oil to every 100 pounds of hard gum and which dries to a very hard, dense film capable of being rubbed to a high polish, the second, or "Finishing Varnish," contains about 25 gallons of oil to every 100 pounds of gum, and, although slow-drying, produces a very elastic, tough and durable film. Experience has demonstrated the unfitness of "Rubbing Varnish" for exterior purposes, so that in the majority of cases "Finishing Varnish" alone is employed.

The "Surfacer" Process was devised about thirty years ago to reduce the time, labor and expense of the old "Lead and Oil" System. The fundamental difference between the two processes is that the "Surfacer" System omits the lead priming and filling and the "rough stuff" coats, but builds up the surface rapidly by the application of specially prepared paints. The first, or priming, coat is usually a quick-drying varnish containing a very small amount of a mineral silicate. The second, or loading, coat is of much thicker consistency and is a mixture of yellow ochre, white lead and dolomite or other equivalent substances ground in quick-drying varnish. The third coat, frequently known as the leveling coat, is similar to the "rough stuff" of the older process, but is devised to amalgamate with the preceding coats. Three applications of this material are usually made and the entire surface rubbed with block pumice to the desired finish. From this point on, the process is identical with the "Lead and Oil" System, the "Surfacer" Process confining its efforts to the rapid preparation of a surface for the color coat.

The "Color and Varnish" Process is of very recent origin and is a radical departure from the two previously described systems. The fundamental idea of this process is that the fewer the number of coats and the more similar in composition, the more durable will be the final results obtained. With this in view, a combination of coats are applied which are so composed as to prime the wood, prepare a surface and obtain the desired color at the same time. This is accomplished by employing heavy silicate paints, containing the proper color ground in the same kind of varnish, each coat possessing suitable drying qualities for its respective demands. The best results are obtained by the use of dark colors such as green or brown, as the principal ingredient may be ochre, umber or some other natural earth pigment which not only produces the desired shade, but is well adapted for preparing a foundation. The surface so obtained is covered with a coat of the body color ground in varnish followed by one thick coat of finishing varnish.

A fourth process is used to some extent which is really an abbreviation of the "Lead and Oil" Process and consists in priming and filling with lead and oil, but instead of applying "rough stuff," which requires expensive labor in rubbing, the lead coats are brought to a reasonable smooth finish with sandpaper. This process is further improved by tinting the surfacing coats in the direction of the body color so that by the use of dark colors, which are also more permanent than the lighter and more brilliant ones, one coat of color will be sufficient.

Each of the processes above described had its specific faults and virtues, so that no one has completely superseded the other two. The "Lead and Oil" Process if properly applied requires from three to four weeks and the application of ten or more coats. The "Surfacer" Process requires about the same number of coats, but, owing to the quicker drying of the surfacers, requires but two to three weeks for application. The "Color and Varnish" Process is the simplest of all and has been applied with apparently successful results in from six to eight days with an application of four to six coats.

The "Lead and Oil" Process produces very satisfactory results both in appearance and in durability, but the lead undercoats require considerable time for drying, the rubbing of the "rough stuff" necessitates the employment of skilled labor and the number of coats applied involves the expenditure of time and money out of proportion to the value of the actual results obtained. In addition, the process is susceptible to serious faults, such as improperly made "rough stuff" paints which are very brittle and produce cracks on drying which destroy the appearance and durability of the finish. The Japan colors serve no function except coloring and yet involve the expenditure of applying one or more complete coats. The most serious drawback to the employment of this method is that few companies are willing to spend the time and money necessarily involved and attempt to cheapen or hasten the work with consequent injury. The process actually produces too fine a surface for cars, and a certain amount of handsome finish can very properly be sacrificed for greater durability.

The "Surfacer" System is capable of producing excellent results with a smaller expenditure of time, but is little cheaper than the "Lead and Oil" Process, as the specially prepared surfacers are expensive. These paints are claimed to give better results than lead and oil, but owing to their nature are dependent upon the skill and honesty of the manufacturer and afford additional opportunity for adulteration. As the process of finishing on the prepared surface is the same as in the "Lead and Oil" Process, the objection to Japan colors applies with equal force. It is true of both processes that the necessary ex-

penditure of time and money to obtain so handsome a finish is not justified by the demands imposed.

The faults of the "Color and Varnish" Process are not as yet thoroughly understood, as the method is of very recent development and has not been subjected to the test of long-continued service. It should be understood that the aim of this shorter process is durability at the lowest cost, and that appearance is in a measure sacrificed, but it is claimed that the finish obtained is fully as durable as by the older methods, that it is free from many of their faults and that it produces a finished appearance sufficiently good for the purpose. On the other hand, the process is dependent upon specially made paints in which adulteration is difficult of detection, and which if carelessly made are not only short-lived but render more difficult the refinishing of the car. It is also claimed that the body colors employed which are in reality a sort of enamel are very apt to produce checking, but this fault can be avoided by proper manufacture. The system is only applicable to dark colors as the lighter and more brilliant pigments do not possess sufficient covering power, but this is not in itself a failing as the use of dark green and brown colors is rapidly increasing, owing to the greater stability and length of life obtained. In this connection it is of interest to note that the Pullman Company has adopted a brown body color as the most satisfactory shade available, while a large proportion of the railroads both steam and electric employ a color of similar nature.

The foregoing brief description of the methods of car finishing in use indicate the wide variation in the processes employed and the results obtained. It has been shown by actual results that a saving of \$20.00 to \$30.00 can be made on the painting of each car and an increase in life obtained of from 5 to 10 years by the adoption of scientific methods of finishing. It is probable that no one of the methods in use embody the maximum efficiency possible of attainment and in view of the very large amount of money involved it is desirable that the entire subject be given careful study by technical chemists. The improvements in methods up to the present time have originated largely with those concerns interested in the sale of paint materials, and the consumer has accepted the changes with no thorough understanding of the underlying principles. The development of surfacers, and body colors is particularly the work of the chemist, for it necessitates a knowledge of the behavior of the various pigments and vehicles under different conditions, and the limitations imposed by manufacturing conditions. It is the duty of the industrial chemist in this as in all other lines of work to select those portions of the older systems which have proven their value and to develop new materials and methods which will lead to a standardization along the lines of maximum efficiency.

## AFTER-EFFECTS OF CERTAIN PHOSPHATES ON LIMED AND UNLIMED LAND.

By H. J. WHEELER.

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The chief reasons for presenting a few of the many data bearing upon this subject, which have been secured at the Rhode Island Agricultural Experiment Station, are the following: (1) It is an almost universal practice among agricultural writers to caution their readers against liming land where superphosphates are to be applied, upon the ground that the presence of the lime will hasten the reversion of the phosphoric acid, in consequence of which its efficiency will be presumably greatly lessened.

(2) Some recent writers seem to hold that the action of chemical fertilizers is exceedingly fleeting.

(3) There has not been a sufficient appreciation of the occasional importance of liming as an aid in rendering the phosphorus of the soil available to plants.

(4) It is not sufficiently recognized that the availability of roasted iron and aluminum phosphates is dependent in a high degree upon the character of the soil, as concerns its content of calcium carbonate.

(5) The recent energetic advocacy of the employment of finely ground tri-calcic phosphate rock (floats) for agricultural purposes makes it especially important that its real agricultural value for various crops, and under varying soil conditions, should be more fully known.

(6) The great difference in the requirements of individual plants and of their ability to utilize the several phosphates under varying conditions, is not properly appreciated.

(7) The tendency of late to generalize from experiments with soil extracts as to what will result in the field is fraught with danger which should be pointed out.

The results presented here were secured in field experiments which were begun in the year 1894, and which are still in progress. Twenty plats of land, each containing two-fifteenths of an acre, are employed in connection with the experiment. They are separated by three foot-paths at the sides and by wide road-ways at the ends. The entire area of each plat is fertilized uniformly, but before harvesting for the final record, the crop is discarded from a strip three feet wide on each side and six feet wide across each end. The area remaining is then exactly one-tenth acre.

The experiment was begun at the outset by others with the idea of comparing applications representing like money values of the several phosphates. However, it was decided later to fully equalize the quantities of phosphoric acid ( $P_2O_5$ ) applied to each plat, which was finally accomplished in the year 1902. The phosphoric acid applied during that interval

of eight years was equivalent to an average annual application of 82 pounds per acre.

Each year generous applications of nitrogen in nitrate of soda and of potash either in muriate, or in high-grade sulphate of potash, have been made annually to all of the plats of land, at a uniform rate.

The phosphate applications have been duplicated in all cases, the applications in one series having been supplemented by lime while in the other they were not.

The following phosphates have been employed:

Dissolved bone-black.

Dissolved bone.

Acid phosphate.

Fine, ground steamed bone.

Basic slag phosphate ("Thomas" phosphate).

Floats (finely ground, unacidulated, tri-calcic phosphate rock).

Raw (unroasted) iron and aluminum phosphate.

Roasted iron and aluminum phosphate.

No phosphate.

Double superphosphate.

Below are given the yields of three of the many plants which were employed in 1903. These results are selected because they illustrate so well certain features in the preceding outline which it is desired to discuss somewhat in detail.

TABLE SHOWING THE RELATIVE YIELDS, IN POUNDS, OF THREE DIFFERENT CROPS.

Kind of phosphate.	Limed.	Unlimed.
<i>Swedish Turnip:</i>		
Dissolved bone-black.....	256	119
Dissolved bone.....	312	175
Acid phosphate.....	270	107
Fine, ground steamed bone.....	341	245
Basic slag meal ("Thomas" phosphate).....	293	232
Floats.....	110	58
Raw iron and aluminum phosphate.....	1	0
Roasted iron and aluminum phosphate.....	117	1
No phosphate.....	16	1
Double superphosphate.....	245	89
<i>German Golden Millet, weighed green:</i>		
Dissolved bone-black.....	162	143
Dissolved bone.....	177	144
Acid phosphate.....	139	149
Fine, ground steamed bone.....	165	153
Basic slag meal ("Thomas" phosphate).....	148	141
Floats.....	163	146
Raw iron and aluminum phosphate.....	132	109
Roasted iron and aluminum phosphate.....	159	118
No phosphate.....	123	50
Double superphosphate.....	160	82
<i>Mangel Wurzel (Norblon Giant):</i>		
Dissolved bone-black.....	328	3
Dissolved bone.....	380	101
Acid phosphate.....	340	8
Fine, ground steamed bone.....	447	16
Basic slag meal ("Thomas" phosphate).....	362	73
Floats.....	223	0
Raw iron and aluminum phosphate.....	36	0
Roasted iron and aluminum phosphate.....	153	0
No phosphate.....	40	0
Double superphosphate.....	145	1

It will be seen from the foregoing results with the four superphosphates, dissolved bone-black, dissolved bone, acid phosphate and double superphosphate that, excepting with the acid phosphate, the yields of millet were invariably greater where lime had been



used than where it had been omitted. It is readily possible, if the experiments had been conducted on a soil already well supplied with lime in calcium carbonate, that the result would have been exactly the opposite. This soil contained a large amount of lime removable by extraction with hydrochloric acid, yet it lacked carbonate of lime to such an extent that, when moistened, it not only quickly and intensely reddened blue litmus paper, but it also yielded immediately to ammonium hydroxide an abundant and intensely dark extract.

The single instance where liming did not prove helpful, in connection with the acid phosphate, was in the case of the millet, but this was unquestionably a mere chance result for upon making twenty-four direct comparisons in another experiment *where more lime had been used* the same kind of millet was injured by liming in every instance. In fact in this case the amount of lime present was almost up to the limit of benefit, and even approached the limit of endurance, for millet. This was not true, however, of the turnip; and even more particularly of the mangel wurzels. These results show the absolute absurdity of discussing the effect of liming land in connection with superphosphates, or indeed other phosphates, without special reference to the character of the soil involved and to the particular variety of plant to be grown.

Since the final equalization of the phosphates was not effected until the previous spring, this being the second crop grown since its accomplishment, these results throw less light upon the duration of the effect of fertilizers than other data which are to follow.

In this case the first liming of the soil occurred in 1894 at the rate of a ton of slaked lime per acre and the second in 1903 at the same rate. It is evident that, where no phosphate was used, the interval of nine years under continuous cropping must have been sufficient to draw heavily upon the native supplies of phosphoric acid which had been rendered available by liming. Nevertheless the result with the millet, which had been limed not only nearly to its limit of maximum direct benefit, but also to its limit of actual endurance, shows a yield of 50 pounds on the unlimed plat and of 123 pounds on that which was limed. This indicates, therefore, the probability that liming had rendered the phosphorus in the soil of the limed plat more available than it would otherwise have been. In other experiments at the Station, where a great lack of lime and of available phosphoric acid existed at the outset, liming liberated sufficient phosphoric acid to render the application of phosphates unnecessary at least for two or three years thereafter.

No beneficial effect of the liming, upon the availability of the raw iron and aluminum phosphate, was observable in connection with the yields of the turnips,

but there was evidence of some possible benefit<sup>1</sup> in this connection with the mangel wurzels and the millet. When it comes to a consideration of the effect of liming in connection with the *roasted* iron and aluminum phosphate, it will be seen that it was most positive as shown by the millet, and it was striking in the highest degree in connection with each of the other crops.

In regard to the floats it will be seen that the results with the millet, on both the limed and unlimed land, were essentially on a par with those secured with the better of the phosphates. With the turnip the inefficiency of the floats on the unlimed soil was exceedingly great; and though the relative inefficiency was far less on the limed land, it was still most striking. As concerns the mangel wurzels the soil was so deficient in carbonate of lime as to practically inhibit their growth, excepting on two of the plats. On this account it is only in the case of the limed plats, that indications of the value of the floats are afforded. It will be seen here that, excepting the case of the double superphosphate, floats fell in efficiency below all of the other of the better phosphates. The reason for the exception in the case of the double superphosphate may have been its high acidic tendency.

These results show the most striking differences in the ability of the different varieties of plants to utilize the different phosphates; and also the great dependence of this ability upon the character of the soil, as affected by liming.

The great danger, and indeed the utter futility, of attempting to predicate from experiments with any given plant grown in soil extracts or indeed by way of pot culture, as to the ability of the soil to produce crops of various kinds, could hardly be more strikingly illustrated, if one bears in mind the variations with the different crops on the same plats of land.

In order to illustrate especially the duration of the effect of the several phosphates, the yields in pounds of potatoes from one-half of each of the plats (one-twentieth acre) in 1909 are given below. It must be recalled that these yields represent those of the seventh year following that in which the equalization of the applications of phosphoric acid was made, or in other words it is the eighth crop following the last application of phosphates to any of the plats.

Kind of phosphate.	Limed.			Unlimed		
	Large.	Small.	Total.	Large.	Small.	Total.
Dissolved bone-black.....	600	80	680	217	233	450
Dissolved bone.....	607	69	676	344	185	529
Acid phosphate.....	500	34	534	333	186	519
Fine ground steamed bone.....	570	60	630	400	156	556
Basic slag meal ("Thomas" phosphate). 530	62	592	450	130	580	
Floats.....	460	45	505	330	180	510
Raw iron and aluminum phosphate.....	312	35	347	64	180	244
Roasted iron and aluminum phosphate 546	48	594	40	184	224	
No phosphate.....	360	45	405	20	125	145
Double superphosphate.....	560	47	607	123	210	333

<sup>1</sup> The better results may have fallen within the limits of natural variation in the plats.

It is evident from an examination of the *total yields* that liming was highly beneficial in connection with all of the phosphates, excepting the floats, and when the relative production of large and small tubers is considered, great benefit is shown even in that case.

These results further support the earlier observations at the Station to the effect that liming may increase the total yield of potatoes but that even if this is not the case the yield of tubers of large size is usually greatly increased on a soil like that under experiment.

The wide differences in yield shown upon the several plats, when the results are compared with those where no phosphate had been used, show that the after-effect of floats, bone meal, basic slag meal and of all of the superphosphates, is great, and long continued, both on the limed and unlimed land.

As concerns the total yields, it will be seen that where no phosphate was used the crop was nearly three times as great on the limed as on the unlimed plat thus showing a percentage gain far in excess of that in any other case. Taking account of the large tubers it will be observed that the same holds true. Therefore, both the yields of large tubers and the total yields give evidence that liming had probably placed at the disposal of the crop more phosphoric acid than would otherwise have been available.

On the unlimed land the inefficiency of the raw and roasted iron and aluminum phosphates is most striking, whether judged by the total yields or by the yields of large tubers. On the limed land the results with the raw iron and aluminum phosphate were poorer than where no phosphate had been used, but the roasted iron and aluminum phosphate gave results superior to those secured with acid phosphate, basic slag meal, or floats. This furnishes therefore a most striking example of the effect of applications of lime upon the continued efficiency of roasted iron and aluminum phosphate even when the last applications of each were made several years previous.

Notwithstanding that the floats had been drawn upon less heavily in previous years, by virtue of smaller crops, than most of the other phosphates, they proved far less efficient on the limed land than any of the others excepting the raw iron and aluminum phosphate which showed a negative value. On the unlimed land they gave, however, a better result than the dissolved bone-black, double superphosphate or roasted iron and aluminum phosphate, and they proved essentially as efficient as the acid phosphate. Doubtless this may be accounted for in some measure by the tendency of tri-calcic phosphate to correct the acid condition of the soil, in which it was aided by a small amount of carbonate of lime, probably present in the floats. This view is supported by the excellent results with basic slag meal, which contains a considerable excess of lime, and hence can over-

come soil acidity in a greater degree than any of the other phosphates that were employed.

These results with floats, under the conditions existing where no lime was applied, cannot be cited to show that floats are equal in value to the other phosphates, for the reasons that the conditions of the soil were not such as to produce a normal crop under any conditions, as shown by the wonderful improvement in the yields after liming. Furthermore, when more nearly optimum conditions were created, as a result of liming, the floats then became decidedly inefficient in comparison with the other phosphates. This question of optimum conditions, in other respects, is a point in connection with comparative tests of phosphates and discussions of them which deserves great consideration if one hopes to arrive at reliable conclusions.

### A CONTRIBUTION TO OUR KNOWLEDGE OF THE NITROGEN PROBLEM UNDER DRY FARMING.

By F. J. ALWAY AND R. S. TRUMBULL.

The development of so-called "dry farming" or "dry-land farming" on the semi-arid portions of the prairies of North America has introduced problems in soil fertility distinct from those of humid or of irrigated soils. The characteristic feature of dry-land farming, in so far as it relates to the soil, is the practice of bare fallowing to store water in the sub-soil, a practice, well known to cause, in humid regions, a rapid decline in soil nitrogen, the portion removed in the form of crops being only a small part of the whole that is lost. While in the least arid portions of the semi-arid regions certain intertilled crops may be found capable of taking the place of the fallow to some extent, such a change in cultural methods is not likely to lessen in any considerable degree the rate of loss of nitrogen. The use of leguminous crops as green manures has been advised as a substitute for the fallow.<sup>1</sup> The growth of the legumes, however, exhausts more or less of the moisture which fallowing would conserve, thus increasing the supply of nitrogen at the expense of that of water and so defeating the very object of the fallow.

Investigations in dry-land farming on the Great Plains have been undertaken only so recently by experiment stations in the United States that data are not yet available to indicate how serious the nitrogen problem is, how soon it will become acute, or how best to solve it. For twenty-two years, however, an experimental farm has been maintained by the Canadian government at Indian Head, Saskatchewan, and during the whole of this time the practice of bare fallowing has been employed for the conservation of moisture, it having been introduced into the Canadian Northwest by Mr. Angus Mackay, who has been

<sup>1</sup> Chilcott, "Dry-land Farming in the Great Plains Area." Year-book, U. S. Dep't of Agr., 1907.

superintendent of this farm since its establishment in 1887. It has been pointed out that this farm is located in a region properly considered semi-arid and that moisture studies of the subsoil clearly show the function of the summer-fallow.<sup>1</sup>

It is to be expected that the soil nitrogen supply will become an immediate economic problem in some parts of the semi-arid region much sooner than in others. Considering the five widely separated points of Indian Head in Saskatchewan, North Platte in Western Nebraska, Amarillo in Northwestern Texas, Solano in Northeastern New Mexico, and Douglas in Southeastern Arizona, we have a range of 400 per cent. of nitrogen as shown by the accompanying table. The samples analyzed were taken by one of us from the heavier types of soil, and accordingly, from those richest in nitrogen and organic matter. All the samples were composites, taken to a depth of six inches from virgin prairies.

TABLE I.—NITROGEN AND ORGANIC CARBON IN SEMI-ARID SOILS

	Nitrogen. Per cent.	Organic carbon. Per cent.
Indian Head, Saskatchewan.....	0.384	4.20
North Platte, Western Nebraska.....	0.175	2.06
Amarillo, Northwestern Texas.....	0.136	1.37
Solano, Northeastern New Mexico.....	0.161	1.28
Douglas, Southeastern Arizona.....	0.087	0.58

In order to be able to form some idea as to the losses of humus, of total organic matter and of total nitrogen induced by continuous cultivation under semi-arid conditions, one of us visited the Indian Head Experimental Farm in October, 1907, and secured over 70 samples of soil to a depth of six inches from various fields, plots, etc., as well as from the adjacent prairie. In the case of each sample the total nitrogen, the humus and the organic carbon were determined, but in many cases in the results reported below only the averages of series are given. The humus was determined by the Hilgard method and the organic carbon by combustion with copper oxide after the carbonates had been decomposed by treatment with phosphoric acid.

The data in regard to crop yields and the history of the fields have been secured partly from the annual reports of the Canadian Experimental Farms and partly from private information furnished by Mr. A. Mackay.

Shut<sup>2</sup> had shortly before called attention to the fact that while the yield of wheat at Indian Head has not shown any marked diminution, there has been a loss of 0.118 per cent. of nitrogen to a depth of eight inches during twenty-three years of cultivation, while the amount contained in the various grain crops produced during this period he calculated to be less than one-third as much as had been lost from the soil. He did

not determine the organic matter, but, on the basis of his studies of the soils of humid eastern Canada, concluded that the total nitrogen and the organic matter rise and fall together.

The farm was part of the prairie until 1882 when it was all plowed and during the next five years kept in small grain. The whole was kept in clean summer-fallow in 1887, the year the government took possession, since which time the history of the different fields has not been the same.

One field which from 1889-1898 had had the following succession of crops: oats, fallow, roots, barley, fallow, roots, fallow, wheat, oats and fallow, was in 1899 divided in twenty-two one-half acre plots which have since been continuously used for rotation experiments. The character of the rotation is indicated in Table II. Lacustral clay forms the surface of the greater portion of the field, varying in depth from a few inches to three feet. The remainder of the surface consists of boulder clay, or till, which also everywhere underlies the lacustral clay. The fallowing has consisted of one plowing early in June followed by three or four cultivations during the summer, this being sufficient to keep down all grass and weeds. Where one cereal crop has been followed by another, or by a legume or by rape, the stubble has been plowed in late summer or in autumn, and in the following spring harrowed and plowed again before seeding. The rape and leguminous plants have been turned under when

TABLE II.—HUMUS, NITROGEN AND ORGANIC CARBON IN SURFACE SIX INCHES OF SOIL OF THE ROTATION PLOTS.

Soil and Plot No.	Rotation. 1899 1900 1901 1902 1903 1904 1905 1906 1907	Humus. Per cent.	Nitrogen. Per cent.	Organic carbon. Per cent.
1 Wheat, oats, soy beans.....	2.49	0.307	3.15	
2 Wheat, wheat, peas.....	2.13	0.276	2.77	
3 " oats, tares.....	1.92	0.251	2.52	
4 " wheat, red clover.....	1.90	0.259	2.56	
5 " barley, alsike and alfalfa.....	1.88	0.263	2.57	
6 Peas, wheat, wheat.....	2.05	0.265	2.68	
7 Tares, wheat, oats.....	2.07	0.264	2.83	
8 Soy beans, wheat, oats.....	1.78	0.244	2.36	
9 Red clover, wheat, wheat.....	1.79	0.219	2.18	
10 Alsike and alfalfa, wheat, barley ..	2.05	0.278	2.89	
11 Rape, wheat, fallow.....	1.92	0.262	2.59	
12 Wheat, wheat, fallow.....	2.00	0.298	2.98	
13 " oats, fallow.....	1.94	0.258	2.56	
14 " barley, fallow.....	1.87	0.254	2.61	
15 " wheat, oats.....	1.91	0.267	2.70	
16 " wheat, barley, oats.....	2.21	0.272	2.81	
17 Oats, soy beans, wheat.....	2.10	0.275	2.79	
18 Wheat, peas, wheat.....	2.05	0.271	2.79	
19 Oats, tares, wheat.....	2.03	0.263	2.69	
20 Wheat, red clover, wheat.....	1.93	0.272	2.77	
21 Barley, alsike and alfalfa, wheat.....	1.93	0.265	2.80	
22 Rape, fallow, wheat.....	2.00	0.260	2.68	
Averages of above:				
1-22 All rotation plots.....	2.01	0.266	2.69	
1, 8, 17 Wheat, oats, soy beans.....	2.12	0.275	2.72	
2, 6, 18 Wheat, wheat, peas.....	2.08	0.271	2.75	
3, 7, 19 Wheat, oats, tares.....	2.01	0.259	2.68	
4, 9, 20 Wheat, red clover and wheat.....	1.87	0.250	2.50	
5, 10, 21 Wheat, barley, alsike and alfalfa ..	1.95	0.269	2.75	
11, 12, 13, 14, 22 Fallow every third year ..	1.95	0.266	2.68	
15, 16 Wheat, oats or barley every year ..	2.06	0.269	2.75	
Fifteen plots, cereal, cereal, legume.....	2.01	0.265	2.69	
Seven plots, no legumes.....	1.98	0.267	2.70	

<sup>1</sup> *Am. Chem. Jour.*, 31, 880 (1906) *Jur. Agr. Sci.*, 2, 333 (1908); *Bull.* 130, Bureau of Plant Industry, p. 17 (1908).

<sup>2</sup> Address of the chairman of the Section of Agr. Chem. at the Toronto meeting of the American Chemical Society, June, 1907. *Science*, N. S., 26, 661, p. 265 (1907).



they have appeared to have reached their heaviest growth.

The most striking result of the analyses is the lack of any apparent connection between the composition of the samples and the treatment received by the different plots during the last nine years. No. 1, the sample highest in humus, nitrogen and carbon, is from a plot on which three crops of legumes have been plowed under, while the samples showing the least of the same constituents, *viz.*, 8 and 9, are likewise from plots on which three crops of legumes had been plowed under. A comparison of the averages shows no distinct difference between the fifteen plots on which legumes had been used as green manure and the other seven.

That an explanation of the differences between the different plots is possible is evident from the data in Table III. Suspecting that distinct differences might be found between different individual samples from the same plot, according as to whether they were from the till or from the lacustral clay, ten individual samples from rotation plot 14 were kept separate and analyzed. Till forms the surface of the west third of this plot and of an isolated area near the center, while the east end has a surface of typical lacustral clay. Near the edge of this area of lacustral clay and about twenty feet within it, five samples, 24 to 28, were taken at intervals of ten feet in a north and south line, and, beginning twenty feet west of 26, five samples, 29 to 33, were taken at intervals of eight feet in an east and west line. While 29 and 30 are really typical of neither type, being intermediate between the two, 31 to 33 are quite representative of the till, being from the isolated area above mentioned, and 24 to 28 are fair samples of the lacustral clay.

TABLE III.—HUMUS, NITROGEN AND ORGANIC CARBON OF INDIVIDUAL SAMPLES FROM THE SAME PLOT.

Soil No.	Humus Per cent.	Nitrogen. Per cent.	Organic carbon. Per cent.
24 Lacustral clay .....	2.30	0.291	3.27
25 " " .....	2.26	0.268	3.19
26 " " .....	2.29	0.282	3.01
27 " " .....	2.28	0.278	3.18
28 " " .....	2.28	0.278	3.08
Average lacustral clay.....	2.28	0.279	3.15
29 Boulder clay.....	2.03	0.278	2.85
30 " " .....	1.94	0.263	2.77
31 " " .....	1.67	0.231	2.43
32 " " .....	1.62	0.227	2.29
33 " " .....	1.57	0.221	2.33
Average Boulder clay.....	1.77	0.244	2.53

The samples of lacustral clay are richer in humus, total nitrogen and carbon than are those of till. From the differences found between the two types of soil on the same plot, it seems probable that the differences found between the different plots should be attributed chiefly to the varying amounts of the two types of surface soil.

Samples were secured from other fields and also from tree rows which had for the preceding 15 years been under continuous bare cultivation. These rows

of trees were planted along the lanes in 1892 and since that time the soil for a distance of twelve feet on each side of the trees has every summer been plowed and cultivated sufficiently to prevent the growth of grass or weeds. A summary of the results are given in Table IV.

TABLE IV.—RELATION OF COMPOSITION OF SURFACE SIX INCHES OF SOIL TO CULTIVATION.

No. of samples.	Cultivation.	Total Organic		
		Humus.	Nitrogen.	carbon.
		Per cent.	Per cent.	Per cent.
6	Virgin prairie.....	2.84	0.384	4.20
2	In cultivation 7 yrs., in grass 18 yrs.....	2.75	0.384	4.05
2	" " " " " 9 yrs.....	2.46	0.367	3.82
2	" " " " " 4 yrs.....	2.25	0.303	2.10
22	" " " " (Rotation plotfield).....	2.01	0.266	2.68
6	Tree strips; in ordinary cultivation			
	10 years, in bare cultivation 15 yrs .	2.12	0.274	2.84
6	In cultivation in fields adjacent to tree			
	strips.....	2.34	0.326	3.35

It is impossible from the data on hand to satisfactorily estimate the original composition of the virgin prairie where lacustral clay occurs.<sup>1</sup> The numbers given in the first line of the table are the averages of samples from the boulder clay and from the lacustral clay summits. The numbers are certainly too low because samples from some fields long under cultivation give slightly higher percentages than these. On soil where grass (in this case mixed with clover) has grown for 18 years, following 7 years of cultivation, no distinct loss is to be observed. The longer the fields have been in grass the less has been the decline. Where no grass at all has been grown the loss is greatest. Continuous bare cultivation in the tree rows has caused greater losses than where bare cultivation (fallow) and cropping have alternated. The extreme loss is probably about one-third of the original amount of all three constituents.

The data showing the effect upon the yield of wheat produced by replacing the summer-fallow by a leguminous crop plowed under as a green manure have been obtained chiefly from the field of rotation plots described above (Table II). A summary of the results is given in Table V. Judged by its crop-producing power, this field was very uniform in 1899, the yield of the 12 plots of wheat ranging only from 35 bushel 20 lb. to 36 bushel 16 lb. per acre. The data for wheat after legumes in 1899 are from a series of half-acre plots in another field. On account of the little data on the yields after fallow in the rotation field there are given in the table the averages of all field lots of the standard varieties grown on summer-fallowed land. There being no field or half-acre plots of wheat after fallow in 1900 it has been necessary to employ the yield of a smaller plot. In 1902 the wheat after fallow on the three rotation plots was injured so seriously by rust that the yield was lower (20.3 bushel per acre) and the quality poorer than on any other plot or field on the farm. Accordingly this yield should not be used in such a comparison.

<sup>1</sup> Alway and Vail, THIS JOURNAL, 1, 17 (1909).

TABLE V.—YIELD OF WHEAT PER ACRE AT INDIAN HEAD AFTER FALLOW, AFTER LEGUMES PLOWED UNDER, AND AFTER WHEAT

Year.	After fallow,				After leguminous green manures.		After wheat, oats and barley.	
	Field lots.		Check plots.		No of 1/2 acre plots.	Yield, bu.	No of 1/2 acre plots.	Yield, bu.
	Acres.	Yield, bu.	No of 1/2 acre plots.	Yield, bu.				
1899	16	32.7	13	35.9	6	34.5	1	28.9
1900	0	..	1 <sup>2</sup>	27.0	5	14.9	4	5.4
1901	17	49.2	1	44.7	5	43.1	2	38.4
1902	40	33.4	3	.... <sup>1</sup>	5	24.9	4	25.5
1903	26	35.8	0	....	5	23.8	4	15.9
1904	44	39.3	1	36.0	5	34.5	2	30.2
1905	44	40.0	3	35.3	5	30.0	4	23.1
1906	45	30.5	0	....	5	20.7	4	16.5
Average.	34.6	..	....	..	..	28.3	..	22.9

In two years, 1899 and 1901, when the previous harvest had been followed by exceptionally wet weather, the yield after legumes was about the same as that after fallow, the autumn rainfall probably having been sufficient to fully charge with moisture the subsoil of all the fields. In the other years the legumes, by exhausting the water of the subsoil, lessened the yield of the succeeding crop. Wheat has given a lower yield when sown on wheat stubble than after legumes, chiefly because the soil has been left drier in the autumn, although partially, probably because the supply of available nitrogen has been less. Even in the case of the two wet years mentioned, the difference in yield is considerable.

The data in Table VI seems sufficient evidence that, notwithstanding a decline of 30 per cent. or more in soil nitrogen, this element has not yet become a limiting factor in the yield of wheat on fallowed land at Indian Head. The table gives the yield of Red Fife wheat both without any fertilizers and with 100 lbs. and 200 lbs., respectively, of sodium nitrate. The plots were on fallowed land in every case, soil not previously fertilized being taken each year. In 1903 all the plots in the fertilizer experiments were so badly injured by rust that the crop was not weighed. The average yields of the three plots for the remaining six years were practically the same. No trials are reported of the use of nitrates on wheat sown on stubble.

TABLE VI.—YIELDS OF WHEAT AT INDIAN HEAD WITH AND WITHOUT NITROGEN FERTILIZERS.

Year.	No fertilizer.		100 lbs. NaNO <sub>3</sub> .		200 lbs. NaNO <sub>3</sub> .	
	Straw, cwt.	Grain, bu.	Straw, cwt.	Grain, bu.	Straw, cwt.	Grain, bu.
1900	17.4	27.7	17.6	27.3	17.6	27.3
1901	66.0	62.7	59.2	61.3	54.8	58.7
1902	37.6	29.2	31.6	28.0	38.8	30.7
1904	28.6	26.3	30.4	28.7	26.4	23.0
1905	72.4	42.7	62.8	42.0	54.0	43.3
1906	48.0	35.3	62.4	38.0	52.4	38.0
Average.	45.0	37.3	44.0	37.5	40.7	36.9

There are two distinct causes of a lowering of the content of organic matter, humus, and nitrogen of cultivated soils at Indian Head, *viz.*, the oxidation of the organic matter and the erosion of the surface soil

by the wind. The deeper the layer of soil is, the lower is the content of humus and nitrogen; accordingly, erosion by the wind will have an effect upon the humus and nitrogen content similar to that of cultivation and may seriously affect the value of any such soil study as this.

The seriousness of the nitrogen problem for the semi-arid region as a whole is evident when it is considered that the loss in 25 years at Indian Head has been almost equal to the total percentage in the virgin soils of northwestern Texas and to much more than that in the virgin soils of Southern Arizona. Further, the use of a theoretically good rotation with leguminous green manures over a period of nine years has failed to have any appreciable effect in checking the rapid loss of soil nitrogen, while it has greatly lessened the yield of grain.

## SUMMARY.

In a comparison of 22 rotation plots no distinct relation has been found between the composition of the soil and the nature of the rotation. In a long cultivated field the till was found poorer in humus, nitrogen and organic carbon than the lacustral clay. The amounts of the above three constituents found in any of the plots depend more upon the relative proportions of the two types of soil occurring on the plot than upon the previous treatment.

The longer the fields have been kept in grasses mown for hay, the less has been the change in composition of the soil. Continuous bare cultivation along tree rows has caused greater losses than the alternation of fallow and crop in the adjacent fields. The extreme loss of nitrogen, humus and organic carbon in 25 years is about one-third of the amounts originally present in the prairie. This loss of nitrogen is not sufficient, however, to cause nitrogen to have become a limiting factor in the yield of wheat on fallowed land at Indian Head.

Attempts to substitute for the bare fallow various leguminous crops, which have been plowed under, have decreased the yields of wheat. The lowered yields are evidently due to the drying out of the soil by the leguminous crop. In the exceptional years when the rainfall of autumn has been very heavy the yields after legumes have been as high as after fallow.

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## NITROGEN AND CARBON IN THE VIRGIN AND FALLOWED SOILS OF EASTERN OREGON.

By C. E. BRADLEY.

Received January, 19, 1910.

The great wheat belt of Eastern Oregon is characterized by a silt loam soil. The deposits are of volcanic origin and are remarkably uniform in structure even to considerable depths. The rainfall in this

<sup>1</sup> Two-acre fields.

<sup>2</sup> A fortieth-acre plot.

<sup>3</sup> Badly injured by rust.

region is light, varying from 6-15 inches in different localities.

The general composition of this soil is given in the following partial analyses reported in Table I, the results being calculated to the moisture-free sample. 99.2 per cent. of this soil passes a 0.5 mm. sieve. It reacts mildly alkaline from the carbonate of lime present.

TABLE I.

	Total Per cent.	Soluble 1.115 HCl Per cent.
SiO <sub>2</sub> .....	62.85	0.34
K <sub>2</sub> O.....	1.63	0.74
CaO.....	4.52	3.05
MgO.....	1.94	1.66
Mn <sub>2</sub> O <sub>3</sub> .....	0.04	.....
Fe <sub>2</sub> O <sub>3</sub> } Al <sub>2</sub> O <sub>3</sub> }	8.47	8.37
P <sub>2</sub> O <sub>5</sub> .....	0.30	0.21
N.....	0.110	.....
Volatile.....	8.37	.....

The effect of long and constant cropping with wheat by the fallowing process has been proven to be destructive to soil nitrogen<sup>1</sup> when carried on under humid conditions. Determination of total nitrogen on a number of these semi-arid wheat soils, however, revealed the fact that very slight differences exist between the nitrogen content of the virgin soils and those which have been farmed for a quarter of a century. In view of this fact it was thought that a comparison of the carbon content of these soils would be of interest as illustrating changes which may have taken place in their organic matter under cultivation.

TABLE II.

No.	Description.	Total nitrogen Per cent.	Nitrogen de- crease per cent	Organ carbon mg. per gms. per cent	Organ carbon decrease Per cent.	Inorgan. car- bon mg. per gram.	Inorgan. car- bon decrease Per cent.
45	Virgin, surface.....	0.114	.....	15.270	0.229	.....	.....
47	Fallow, surface.....	0.107	-6.1	11.731	23.2	0.142	38.4
46	Virgin, subsoil, 18 inches.....	0.081	.....	9.860	0.125	.....	.....
48	Fallow, subsoil, 18 inches.....	0.081	-0.0	7.540	23.5	0.116	7.2
49	Virgin, surface.....	0.101	.....	14.133	0.411	.....	.....
52	Fallow, surface.....	0.102	+1.0	11.150	21.1	0.131	68.1
50	Virgin, subsoil, 18 inches.....	0.094	.....	9.730	0.202	.....	.....
53	Fallow, subsoil, 18 inches.....	0.090	-4.3	7.352	24.4	0.153	24.2
54	Virgin, surface.....	0.098	.....	.....	.....	.....	.....
55	Fallow, surface.....	0.102	+3.9	.....	.....	.....	.....

In Table II are given results of nitrogen and carbon determinations on typical samples of these soils. Nos. 45 and 46 are samples of virgin surface and subsoil and Nos. 47 and 48 are the corresponding soils which have been cultivated for 25 to 30 years, wheat and fallow alternating. Nos. 49 and 50 are likewise virgin samples with 52 and 53 the corresponding soils which have been in cultivation for about 17 years. No. 55 has been farmed about 25 years. These samples were obtained from Umatilla, Morrow, and Sherman counties respectively.

The nitrogen was determined by the regular Gunning method, only traces of nitrates being present.

<sup>1</sup> Ladd, Bulletin 24, North Dakota Experiment Station. Snyder, Bulletin 70, Minnesota Experiment Station.

Total carbon was estimated by the method of Parr.<sup>1</sup> The soil fusion obtained by combustion with sodium peroxide and powdered magnesium in the calorimeter bomb was decomposed with sulphuric acid and the liberated carbon dioxide measured in a Parr apparatus by absorption with caustic potash. Carbon as carbonates was estimated in a separate portion of soil by direct decomposition with acid in the apparatus and measured as before.

Hilgard<sup>2</sup> has pointed out that oxidation in the arid soils effects the humus carbon and hydrogen particularly and that the nitrogen content of the arid humus may thus increase. Hilgard and Jaffa<sup>3</sup> show that the arid humus contains on the average three and a half times as much nitrogen as does the humid.

It is evident from the above results in Table II that while the percentage of nitrogen in these soils has remained practically constant under continual cropping for, in extreme cases, 25 years, there has been a marked decrease in the carbon or organic content.

With an average yield of 20 bushels of wheat approximately 30-40 pounds of nitrogen would be removed by grain alone from each acre annually. As little or no waste by leaching occurs on account of limited rainfall, it would seem that fixation of nitrogen might take place to the extent of maintaining practically a nitrogen equilibrium. The soils furthermore are warm, porous, and mildly alkaline with calcium carbonate, and when sufficient moisture is present would furnish a good medium for bacterial growth.

Credit is due Mr. B. Pilkington for the analytical determinations involved in this work.

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## SPANISH PAPRIKA.

By ARTHUR LOWENSTEIN AND W. P. DUNNE.

Received January 7, 1910.

A paper on this subject was presented by one of us at the New Haven meeting of the American Chemical Society in 1908, an abstract of which appeared in Science.<sup>4</sup> Coincident with the presentation of this paper was one on the "Composition of Known Samples of Paprika" by Doolittle and Ogden.<sup>5</sup> That this subject appears to be of considerable general interest in this country is evidenced by the fact that since this time coöperative work on this material was conducted by the referee on spices of the Association of Official Agricultural Chemists.<sup>6</sup> The chief point at issue in these papers has been the determination of the iodine number of the non-volatile ether extract, and its value in the detection of adulteration in paprika.

<sup>1</sup> J. A. C. S., 26, 294-1640. Bulletin 107, revised, Bureau of Chemistry, page 234.

<sup>2</sup> Soils, page 124.

<sup>3</sup> Report of Cal. Experiment Station, 1892-4.

<sup>4</sup> August 7, 1908.

<sup>5</sup> J. A. C. S., 30, 1481 (1908).

<sup>6</sup> Proc. A. O. A. C., Bulletin 122, 35 and 213.



The title of this paper should properly be "Spanish Pimiento" as this is the name by which it is known in its native country. The term "Paprika" is of Hungarian origin, and according to a ruling made by the U. S. Government authorities within the last year, the Hungarian product alone may be called "Paprika."

In order to obtain reliable data, for the purchase of this material, samples of known origin were obtained direct from the growers in Spain—chiefly those residing in the province of Murcia. The whole pods only were used in this investigation. The seeds were carefully separated from the shells and analyses made separately on each. The percentage of seeds was determined and found to be on an average about 40 per cent. by weight.

The forms of adulteration of Spanish pimiento encountered in the ground material are added oil (usually olive oil) seeds, stems, sweepings and artificial color. The latter can be readily detected and is not as common as formerly. In regard to the presence of seeds at the present time most all of the ground product contains seeds in varying proportions. The growers maintain that seeds are not an adulteration when present in quantities normal to the whole pods. The higher grades contain a smaller proportion of seeds than this quantity, while low grades are apt to contain a much

larger proportion, in which case they unquestionably constitute adulteration.

Paprika is graded commercially by its degree of color. Seeds impart no color and consequently lower the shade. Olive oil on the other hand intensifies the color and thus makes lower grades appear better than they really are. It is claimed that the oil is added to preserve the color of the paprika, and there seems to be some merit in this claim as the coloring matter of the various species of *Capsicum annuum*, L. is very unstable to light and heat. However, it has been our experience that Spanish pimiento packed in hermetically sealed tins maintains its original color for a long period, whereas this same material shipped in burlap bags and stored loses much of its color and depreciates in value. It seems only proper that if oil is added it should be plainly stated on the label. While the addition of olive oil apparently intensifies the color of the ground material, the actual color of the paprika is in reality lowered and this can be revealed by making a tintometer reading of the alcoholic extract, a test which we find very valuable in selecting paprika prior to purchase.

The proportion of seeds may be roughly approximated from a study of the non-volatile ether extract, the ash and the iodine number of this extract. It will be noted from the appended table that the presence

TABLE I.—SPANISH PIMIENTO OF KNOWN PURITY.

Lab. No.	Description.	Loss at 100° C. volatile, per cent.	Total ash, per cent.	Ash soluble in water, per cent.	Ash insoluble in water, per cent.	Total ether extract, per cent.	Volatile ether extract, per cent.	Non-vol. ether extract, per cent.	Alcoholic extract, per cent.	Crude fiber, per cent.	Butyrefract. reading, 30° C.	Iodine number.		
												Yel. 20	Red. 40	Method of extraction.
45187a	Shells	5.87	8.77	7.57	0.24	6.39	0.67	5.72	13.50	19.60	off the scale			Doolittle-Ogden modified
45187b	Seeds	5.48	3.22	1.22	0.14	22.03	0.52	21.51	22.70	27.99	65°	no color	no color	"
45188a	Shells	12.32	9.25	8.65	0.31	6.37	0.75	5.62	23.34	18.70	off the scale	20	43	"
45188b	Seeds	5.82	3.84	1.83	0.2	20.97	0.6	20.37	24.70	27.39	64°	no color	no color	"
45189a	Shells	.....	10.00	9.50	0.1	6.80	0.25	6.55	18.05	24.10	.....	20	23.5	"
45190a	Shells	15.90	9.50	8.78	0.1	5.82	0.7	5.12	24.60	20.05	.....	.....	.....	Petroleum spirit
45190b	Seeds	6.63	3.40	.....	0.04	20.36	0.27	20.09	21.30	29.45	64°	no color	.....	.....
45190c	Stems	3.66	.....	.....	.....	3.24	0.3	2.94	.....	31.26	.....	.....	.....	.....

TABLE II.—INFLUENCE OF ADDING KNOWN AMOUNTS OF OLIVE OIL.

45191a	Commercial ground pimiento	17.95	7.35	.....	0.18	13.18	0.75	12.47	26.98	18.60	72°	20	16.5	Petroleum spirit	119.4
45191b	5% olive oil added	.....	.....	.....	.....	.....	.....	16.80	20.00	17.87 (calc.)	65°	20	12.5	"	116.9
45191c	10% olive oil added	.....	.....	.....	.....	.....	.....	21.18	18.75	16.74 (calc.)	64°	20	11.2	"	114.6
45191d	Olive oil used	.....	.....	.....	.....	.....	.....	.....	.....	.....	59°	.....	.....	.....	83.5

TABLE III.—ANALYSES OF SOME COMMERCIAL GROUND PIMIENTO.

45192	Non-vol. extract dried to constant wt. in air oven	8.40	7.0	5.65	0.19	19.31	1.35	17.96	27.04	17.0	67.5°	.....	.....	Petroleum spirit	111.7
45193	"	14.10	7.32	6.59	0.25	13.76	1.00	12.76	20.14	18.74	69°	.....	.....	"	113.3
45194	"	15.87	7.46	.....	.....	12.87	0.55	12.32	28.35	19.02	.....	20	20	.....	.....
45195	"	10.72	7.50	.....	0.4	16.35	0.4	16.45	26.10	.....	.....	20	17	Doolittle-Ogden modified	119.5

of seeds increases the ether extract, and lowers the ash, iodine number, refractive index and color.

The presence of stems increases the ash and fiber and reduces the ether extract, and lowers the iodine number and color.

Olive oil increases the ether extract, lowers the iodine number, ash, refractive index, fiber and color.

*Iodine Number of Non-Volatile Ether Extract—Methods.*—In our opinion the point of prime importance in this connection is the proper determination of the non-volatile ether extract. We have shown in another paper<sup>1</sup> the influence of the method of heating on the composition of the non-volatile ether extract of spices. It is sufficient to say at this point that "heating to constant weight at 110° C." as stated in the official method of the A. O. A. C., gives non-volatile ether extracts of varying composition and consequently of varying iodine absorption capacity. We think that this point more than any other will account for the widely divergent results obtained by the different analysts, in the coöperative work of the A. O. A. C. reported by Winton. We also observe that this point has given rise to the opinion that satisfactory duplicate iodine numbers cannot be obtained on two portions of a sample of paprika, extracted by the A. O. A. C. method. It is our experience that satisfactory duplicates can be obtained if the extraction is carefully conducted and the extract brought to constant weight in a vacuum oven. In the case of paprika, heating to constant weight in an ordinary air oven at 110° C. not only frequently completely decolorizes the extract but oxidizes it so much that a considerable portion of it will no longer dissolve in chloroform when the iodine number is determined.

In our early work on paprika, we extracted a ten-gram portion of the ground sample with redistilled petroleum spirit (88°–90° B<sub>e</sub>.) repeatedly in a cylinder and then transferred to a filter and continued washing until the extract was colorless. Then the petroleum spirit was distilled off, volatile extractives removed, and a sufficient quantity of the non-volatile extract was thus obtained to make duplicate iodine determinations and a refractive index reading. Later, after the publication of the paper by Doolittle and Ogden, and the modification of their method of extraction by W. Denis, we adopted this modified method as more convenient. It might be noted that the petroleum ether extraction method gives results which check within 1 per cent. with this latter method. Later we found that we could obtain very satisfactory results by using the non-volatile ether extract—obtained by the regular A. O. A. C. method (using a 5-gram sample)—when the precautions above mentioned were employed. By dissolving this extract in chloroform and making to a definite

volume, satisfactory duplicate iodine values can be determined on aliquots. This latter method we find most convenient as it saves a separate extraction. The Hanus method was employed in making all iodine numbers.

In connection with the iodine value it might be interesting to call attention to the iodine number of the shells of No. 45189a, which was an old sample of very inferior quality at the time the determination was made, although it was pure Spanish pimiento. It will be noted that it has the characteristic high ash—ether extract and fiber are normal—but the extract has oxidized with consequent lowering of the iodine number. Its inferior quality will be revealed from a comparison of its color reading with that from fresh, high-grade shells, No. 45187a.

*Refractive Index.*—It is interesting to note that while we have been able to read the degree of refraction of the non-volatile ether extract of all ground commercial paprika on the butyro-refractometer, that when we came to make the reading on the shells only, we found that the reading was too high for this scale and had to be read on the Abbé instrument. Therefore, while the refractive index, or better the butyro-refractometer reading in itself is of but little value in detecting adulteration with oil, it will be seen from the appended table that it is of value in conjunction with the other tests.

*Tintometer Reading.*—We have found either the Lovibond or Duboscq instrument convenient for measuring the color of the extract of paprika. We employ the alcoholic extract as obtained by the official A. O. A. C. method, taking 10 cc. of this extract and diluting to 100 cc. with 95 per cent. alcohol.

TABLE IV.—COMPARISON OF THE INFLUENCE ON THE IODINE NUMBER OF DIFFERENT METHODS OF EXTRACTION, TIME OF EXTRACTION, AND METHOD OF HEATING NON-VOLATILE ETHER EXTRACT.

Lab. No.	Time of extraction, hours.	Method of extraction.	Method of heating.	Iodine No.
45187a	....	Petroleum ether	Vacuum oven 10 cm. Hg.	a { 137.2
45187a	....	Doolittle-Ogden modified	" "	a { 137.2
45187a	24	A. O. A. C.	" "	b { 138.0
				a { 138.3
				b { 137.7
45187a	100	Continuous extraction with anhydrous alcohol-free ether	" "	123.6
45187a	100	Continuous extraction with petroleum spirit 88–90° B <sub>e</sub> .	" "	120.9
45188a	24	A. O. A. C.	" "	130.2
45188a	24	A. O. A. C.	Official A. O. A. C. to constant wgt. in air oven at 110° C.	123.0

The color readings given in the table were made on this basis. It will be noted that olive oil and seeds lower the color reading very markedly, and we find this determination of great help in selecting paprika,

<sup>1</sup> THIS JOURNAL, 2, 47.

and in judging whether goods received are equal in quality to samples originally submitted.

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## THE PREPARATION OF CURD FROM BUTTERMILK.<sup>1</sup>

By J. L. SAMMIS.

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The filtration of colloidal precipitates is often a difficult operation. The difficulty of collecting curd from heated buttermilk by filtration has heretofore prevented the practical creamery man from preparing from buttermilk anything resembling the well-known cottage cheese made from skim milk. It has long been known<sup>2</sup> that curds from skim milk or from mixtures of skim milk with not too much buttermilk can be easily collected by filtration on cheese-cloth, but no reliable method has been accurately described<sup>3</sup> for handling buttermilk alone, desirable as such a method is.<sup>4</sup>

Previous attempts at this University to obtain a filterable curd from pure buttermilk and to produce from it a product having any desired moisture content and consistency from creamy to dry and pasty had progressed only so far as to show that a creamy product "Buttermilk Cream,"<sup>5</sup> could sometimes be obtained, but not far enough to develop a reliable method for its manufacture or for controlling its moisture content. Neither the yield nor the moisture content of the product is stated.

The present study was begun in September, 1909, at the suggestion of Professor Farrington, of the Dairy Department. The following described method<sup>6</sup> was devised by the writer and it has been used daily for about four months at the University Creamery with uniform success.

It includes special heat treatment of the buttermilk for two purposes: first, to obtain the curd in a form which can be readily filtered on cheese-cloth, and, second, to regulate the moisture content of the curd so as to give it any desired consistency. Buttermilk of 0.5 to 0.6 per cent. acidity, made by churning either raw or pasteurized cream, is placed in any suitable container provided with means for heating. The buttermilk is stirred and heated to 25°–26° C., is then covered and left undisturbed at this temperature for 1½ to 2 hours.

The purpose of this operation is to bring the butter milk quickly to a temperature at which it will slowly

coagulate and to let it become quiet before coagulation occurs. As the granules of curd separate from the quiet liquid, they cohere forming a fragile floating mass, which shrinks and becomes tougher, as the whey is expelled, during the next two hours. If stirred too long or heated too high at first, the buttermilk will curdle while in motion, and the grains of curd will not cohere or float but will settle in the form of a fine flocculent precipitate which can not be filtered on cheese-cloth.

Then shrunken cohering mass is stirred gently at the end of two hours, while heating to 38, 55, or 60° C., and then left quiet to settle. This leaves the curd in the form of coarse flocks which will easily filter on cheese-cloth at any time thereafter. The higher the temperature of this second heating, the drier the final product will be after draining. The second heating causes more complete dehydration of the curd, and the whey thus formed is removed in the final draining process.

If the second heating be for 15 minutes at 38° C. the final product is a thick creamy fluid with a glazed surface containing about 82 per cent. of moisture, shown at the left of the figure. It has been called "buttermilk cream," as stated above.



"Buttermilk cream" and "Buttermilk cheese"

If the second heating be continued for 1 hour or more at 55° C. before draining on cheese-cloth, the final product resembles a good quality of cottage cheese in appearance, as shown at the right of the figure, and the moisture content is about 77 per cent. If the second heating be continued at 60° C. for 3 hours, the appearance of the product after draining is practically the same as when 55° is used, but the moisture content is reduced to about 72 per cent. and the yield is somewhat reduced. In any case, after the second heating most of the clear whey can

<sup>1</sup> Published by permission of the Director of the Wisconsin Agricultural Experiment Station.

<sup>2</sup> See Knoch, *Die Magermilch Verwertung*, Leipzig, 1903, p. 90–91.

<sup>3</sup> Anonymous, *Heard's Dairyman*, 28, 86, 1897.

<sup>4</sup> See R. K. Duncanson, *THIS JOURNAL*, 1, No. 8, 602.

<sup>5</sup> "Buttermilk Cream, a New Product," *Heard's Dairyman*, 40, 20, March, 1910.

<sup>6</sup> From the advance sheets of this paper, E. H. Farrington has published part of the method in *Heard's Dairyman* for Dec. 31, 1909, p. 1424, from which it was copied in other dairy papers.



be decanted from the curd, which nearly all sinks after being stirred and heated the second time. The remaining curd and whey is poured at once into a cheese-cloth bag, returning the first portions which run through, till the drippings are water-clear. The curd in the bag is stirred occasionally since the layer next the cloth drains fastest, and delays the draining of the interior of the mass. It is left over night in the bag. In the morning it is seasoned with 1 per cent. of salt and, if desired, with 0.1 per cent. of white pepper or in other ways. The dry product, which may be called *buttermilk cheese*, is eaten like cottage cheese. It can also be used as a diluent for other materials, as an article of food; or with preservatives, it can probably be used as a basis for various preparations.

The curd from buttermilk differs in one respect from skim milk curd or cottage cheese. Buttermilk curd is always exceedingly fine-grained in its ultimate texture, so that it can be quickly rubbed to a paste with water between the fingers.

Further study is in progress. It is hoped that the method described for precipitating and filtering buttermilk curd may be found useful by those who have other colloidal material to filter.

UNIVERSITY OF WISCONSIN, AGRIC. EXPT. STATION,  
January, 1910.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

## THE QUANTITATIVE DETERMINATION OF CANE SUGAR BY THE USE OF INVERTASE.

By C. S. HUDSON.

Received January 17, 1910.

*Introduction.*—The general method now in use for estimating cane sugar is the procedure of Clerget, in which the sugar is hydrolyzed by acid and the resulting invert sugar estimated either by its reduction of Fehling's solution or by the change in optical rotation which results from the hydrolysis. It has long been known that the presence of other hydrolyzable substances with the cane sugar interferes in the determination because the hydrolysis by acid is then not confined to the cane sugar. This method would be greatly improved if some substitute for the acid were known which would hydrolyze the cane sugar without attacking other acid-hydrolyzable substances; it is the purpose of this article to show that the enzyme invertase in most cases fulfils this requirement, and that its use to supplement or even replace acids in the quantitative estimation of cane sugar is of great value in analytical work. The use of the enzyme in studying the sugars which occur so widely distributed among plants is particularly recommended.

*The Preparation of Invertase.*—To prepare a stock solution of invertase, break up five pounds of pressed yeast, which may be either baker's or brewer's yeast,

add 30 cc. of chloroform to it in a closed flask and allow it to stand at room temperature (20°) over night. By the morning the solid mass will have become fluid and it should then be filtered through filter paper, allowing several hours for draining. To the filtrate add neutral lead acetate until no further precipitate forms and again filter. Precipitate the excess of lead from the filtrate with potassium oxalate and filter. To this filtrate add 25 cc. of toluene and dialyze the mixture in a pig's bladder for two or three days against running tap water. The dialyzed solution is colorless, perfectly clear after filtration, neutral to litmus, has a solid content about one-half of one per cent., an ash content of a few hundredths of one per cent., will keep indefinitely in an ice box if a little toluene is kept on its surface to prevent the growth of microorganisms, and is exceedingly active in inverting cane sugar. The invertase solution does not reduce Fehling's solution.

*The Keeping Qualities of the Invertase Solution.*—The stock solution of invertase prepared as described keeps perfectly. A quantity of it has been tested during a period of fifteen months and no change in its general appearance or inverting activity noted. Three other preparations of less age have also shown no appreciable change. All of these solutions have been kept in an ice box and toluene was added in excess of saturation in each case. Another preparation has been observed by H. S. Paine, of this bureau, who found that the preparation did not change in inverting activity during a period of three months. This sample was kept at room temperature (20° to 30°) during the day and in an ice box at night, thus duplicating the conditions which occur where many analyses are carried out each day with the use of the invertase solution.

*The Rotatory Power of the Invertase.*—The stock solutions of invertase have a slight rotatory power and in a 400 mm. tube they give a dextro-rotation of 1.0° V. In the method to be described further on, the inversion of 95 cc. of sugar solution is accomplished by 5 cc. of the invertase solution, and therefore the correction to be applied for the rotation of the invertase solution is 0.05° when the reading is made in a 400 mm. tube or 0.025° when a 200 mm. tube is used. For all ordinary work these corrections are negligible and they can always be accurately determined when the accuracy requires them.

*The Numerical Formula for the Determination of Cane Sugar by Invertase.*—If  $S$  denote the polarization of pure cane sugar before inversion and  $I$  that after inversion, the numerical factor of inversion, which can be found by experiment, is  $I/S$ . This factor varies greatly with the temperature, due to the influence of the latter on the rotation of fructose. H. S. Paine and the author have measured this factor at 20° when invertase is used as the inverting agent

<sup>1</sup> Read at the Boston meeting of the American Chemical Society.

on sugar solutions of 7 per cent. strength and have found its value to be 0.317; similar experiments have given the factor 0.324 for the inversion by hydrochloric acid when the solution is kept at room temperature over night and read in the acid condition. For the same acid solution after neutralization the factor 0.317 was found, showing that it is the acidity which causes the difference between the factors for invertase and unneutralized acid solution. To check this point, the same quantity of hydrochloric acid was added to the solution which had been inverted by invertase and had given the factor 0.317; it was found that its rotation changed immediately to a greater negative value which corresponded to a factor 0.324, thus verifying the above conclusion in a different way. The inversions by invertase which gave the factor 0.317 were made in a solution which had been acidified with acetic acid, as invertase acts only in an acid solution; the two acid strengths of 0.01 and 1.0 normal were used and the factor was found to be the same for both, 0.317. Other experiments have been made in which the solution was weakly acidified with other acids to produce an acid medium in which the invertase would act and for the inversion by invertase in these weak acid solutions (five ten-thousandths normal) the following values of the factor  $I/S$  at  $20^\circ$  were found: Nitric 0.315, sulphuric 0.315, oxalic 0.314, citric 0.314, tartaric 0.320, phosphoric 0.315, arsenic 0.315, hydrochloric 0.315, hydriodic 0.315. The average of these values is 0.315, which is quite close to that given for acetic acid and for the neutralized hydrochloric inversions, 0.317; a difference of four-tenths of a degree in the temperature at which the readings of the inverted solutions were made would account for this variation. Chas. A. Browne<sup>1</sup> has found the value 0.325 for the inversion by hydrochloric acid when the acid solution is read, and the value 0.317 after neutralization, numbers which are practically identical with those given here. Weber and McPherson<sup>2</sup> find at  $20^\circ$  the factor 0.317 for inversions by hydrochloric acid, correction being made for the influence of the acid. L. M. Tolman<sup>3</sup> finds the factor 0.318 for acid inversions, the acid being corrected for, and states that "if an inverting agent could be obtained which had no effect on the invert sugar the question of concentration [influencing the factor] would practically be eliminated. But the elimination of this error would necessitate the determination of a new factor which would in all probability be 141.79 (i. e., 0.3179) or perhaps a little less." Invertase fulfils this requirement and its factor is 141.7. It is thus certain that the factor for the inversion of cane sugar by invertase is considerably less than the factor for the usual hydrochloric acid inversion, that its value at  $20^\circ$  approxi-

mates 0.317 closely and that the difference between the factors for invertase and hydrochloric acid is due to the effect of the acid on the rotatory power of invert sugar. These experiments also prove that the hydrolysis of cane sugar by invertase is a complete one, for just as much invert sugar was formed by the invertase inversion as by that due to the strong hydrochloric acid. The usual formula for the per cent. of cane sugar may therefore be used with the new factor 141.7 when the inversion is carried out by the use of invertase.

$$\text{Per cent.} = \frac{S - 1}{141.7 - T} \times 100.$$

*The Influence of Acids and Alkalis on the Activity of Invertase.*—Invertase acts only in an acid medium, and the slightest alkaline reaction stops its action instantly. Weak alkalinity does not destroy it, however, for if the acidity be restored the invertase resumes its original activity. But it is quite important that the medium be only weakly acid, for invertase is rendered inactive and even destroyed by acidities above hundredth-normal hydrochloric. As this acidity is itself rather weak, it seems best to avoid the use of strong mineral acids entirely in preparing the sugar solution for the action of invertase, and to use in their place a weak organic acid such as acetic, for invertase is quite active in acetic acid of 5 per cent. strength.

In the accompanying figure there is given the measured activity of invertase in solutions of hydrochloric acid and of acetic acid. These activities were found by mixing at  $30^\circ$ , 100 cc. of 0.2 normal (approx. 7 per cent.) cane sugar solution with 5 cc. of the appropriate strength of acid and 5 cc. of a stock invertase solution, and measuring the velocity-coefficient ( $k$ ) of the resulting inversion by the usual formula  $k = \frac{1}{t} \log \frac{R_0 - R_\infty}{R - R_\infty}$  where  $R_0$  is the initial rotation of the solution,  $R_\infty$  the value after complete inversion,  $R$  the rotation at the time  $t$  (expressed in hours), and  $\log$  the common logarithm. Care was taken to make the samples alkaline before each reading of  $R$  in order to stop the action of the invertase

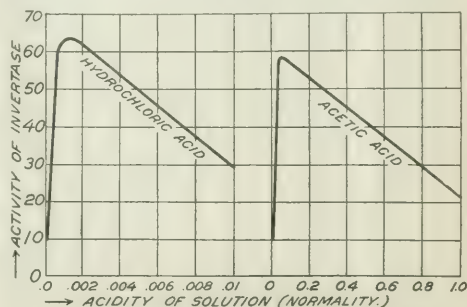


Fig. 1.—Influence of strong and weak acids on the activity of invertase

<sup>1</sup> U. S. Dept. Agric., Bureau of Chem., Bulletin 110, p. 44.

<sup>2</sup> *J. Amer. Chem. Soc.*, 17, 324 (1895).

<sup>3</sup> *Ibid.*, 24, 523 (1902).

and complete the mutarotation of the invert sugar. The figure shows that invertase is active in only a very small range of acidity when the latter is due to a strong acid like hydrochloric, which is almost completely dissociated in solution, but that if a weak acid like acetic is used, its dissociation is so slight that quite strong solutions can be used, without bringing the actual acidity (*i. e.*, hydrogen-ion concentration) up to a strength which is inimical to the action of invertase. As it would be difficult in practical work to adjust the acidity of the solutions very accurately, it is recommended that the solutions be all made acid to litmus with acetic acid, as even a considerable excess of acetic acid will do no harm.

*Directions for Making the Analysis.*—Dissolve 26 grams of the substance to be analyzed for cane sugar in water, clarify with the usual substances (neutral or basic lead acetate or alumina cream or kaolin) and make up to 100 cc. volume at 20°. Filter and read the polarization of the filtrate,  $S$ , for a 200 mm. tube. Remove the excess of lead from the filtrate, if lead has been used as clarifying agent, with sodium carbonate or potassium oxalate and filter. To 50 cc. of the filtrate add acetic acid by drops until the reaction is acid to litmus, add 5 cc. of the stock invertase solution and make up the volume to 100 cc. Add a few drops of toluene to the solution to prevent the growth of microorganisms, shaking so as to saturate and allow to stand at any temperature between 20° and 40° over night. Under usual conditions about six hours time is required to accomplish complete hydrolysis. In the morning bring the temperature to 20° and read the rotation of the solution,  $I$ , for a 400 mm. tube. The percentage of cane sugar present is then calculated by the formula given on page 144. The percentage can also be found by the cuprous oxide reduction before and after inversion by the invertase.

*The Influence of Mutarotation on the Invert Polarizations.*—The temperature does not influence the rotation of glucose but changes that of fructose greatly and the change of rotation lags behind the change of temperature. This lag is due to the mutarotation of fructose and practically disappears in inversions by hydrochloric acid for the reason that the acid is a strong catalyst of the mutarotation. In solutions inverted by invertase the lag for fructose which follows a change in the temperature of the solution lasts about ten minutes at 20°, and care should therefore be used in reading the invertase inversions to see that the rotation remains constant for a few minutes. It is the writer's practice, after the invert reading is obtained, to add a pinch of cane sugar to the solution and observe its rotation for a few minutes; if it gradually changes, showing that the cane sugar added is being inverted, one is certain that the invertase is active and has accomplished a complete inversion over night.

*Tests of the Invertase Method.* 1. *Test on Pure*

*Cane Sugar.*—Direct polarization ( $S$ ) 100°, invert polarization, with hydrochloric acid,  $-33.2$ , consequently the per cent. sugar by Herzfeld's formula,

$$S - I \\ 142.7 - T \times 100 \text{ is } 100.4.$$

The inversion by invertase gave  $I = -31.9$ , and the percentage by the above formula with the constant 141.7 for invertase, as described before, is 100.1. The polarizations in all the tests were made at 20°.

2. *Test on Louisiana Cane Syrup.*—This syrup had been treated with  $SO_2$  in the process of manufacture. Direct polarization was 55.6, invert polarization by hydrochloric acid  $-14.9$ , by invertase  $-13.8$ , giving the percentage of cane sugar by hydrochloric inversion as 53.1, and by invertase inversion 52.7 per cent.

3. *Test on Bagasse.*—S. F. Sherwood of this bureau recently obtained the following percentages of cane sugar in samples of Cuban bagasse, using the hydrochloric acid and also the invertase methods of inversion and determining the invert sugar for both methods by the change of polarization and also by the increased reduction of Fehling's solution.

ANALYSES OF BAGASSE.  
Per cent. cane sugar.

Sample No.	Hydrochloric acid inversion.		Invertase inversion.	
	Polarization.	Reduction.	Polarization.	Reduction.
1	23.6	23.9	23.6	23.3
2	16.4	16.1	15.8	16.0
3	12.4	13.4	13.4	13.3
4	7.2	8.0	8.7	7.7

These three substances, pure cane sugar, cane syrup and bagasse, show practically the same cane sugar percentage by the hydrochloric acid and the invertase methods. There will now be given an example of a very different type of analysis.

4. *Test on the Sotol Plant (Dasylirion Texanum).*<sup>1</sup>—The soluble matter from 26 grams of the whole plant was dissolved to 100 cc. and the polarization  $S$  found to be  $-9.2$ . Inversion by hydrochloric acid gave  $I = -16.5$ , by invertase  $I = -9.7$ . The percentage of cane sugar determined by acid inversion was 5.5, by invertase inversion, 0.4. The analysis shows such a striking disagreement between the two methods that a further determination of the reducing sugar before and after the hydrolyses was made with Fehling's solution. The true carbohydrate composition of this plant was found by this method to be:

	Per cent.
Reducing sugars.....	2.8
Cane sugar (by invertase inversion).....	0.7
Unknown carbohydrate (by acid inversion).....	13.3

Here then is a substance which contains only a trace of cane sugar but a large quantity of a very easily hydrolyzed carbohydrate; further work on the nature of this unknown carbohydrate is in progress.

<sup>1</sup> This interesting plant occurs in the waste dry regions of New Mexico and Texas; a description of it is given in Prof. W. L. Bray's "The Vegetation of the Sotol Country in Texas," Univ. of Texas Bulletin No. 60.



5. *Test on Commercial Glucose.*—A 26 per cent. solution of "mixing glucose," which is prepared by the acid hydrolysis of starch, gave a rotation of  $86.0^\circ$  V. Inversion by hot hydrochloric acid changed this to  $85.2^\circ$ , by cold acid  $85.3^\circ$ . Five drops of invertase solution were added to a third portion and after standing over night its rotation was still  $86.0^\circ$ . The method of manufacture of this mixing glucose by hot acid hydrolysis makes it certain that no cane sugar can be present in it, and the method of analysis in which invertase is employed shows no cane sugar, but the usual acid methods give a slight decrease of rotation. Weber and McPherson<sup>1</sup> have particularly investigated this error in the acid methods of hydrolysis and devised a correction for it, but the invertase method is certainly preferable.

6. *Commercial Glucose with Added Cane Sugar.*—Commercial glucose is frequently flavored with a small quantity of cane syrup to make it more palatable and is then sold for table use. An analysis for cane sugar of such "cane-flavored" glucose gave the following: Rotation of a 13 per cent. solution of the sample in a 200 mm. tube  $75.0^\circ$  V., rotation after inversion with hot hydrochloric acid  $72.7^\circ$ , with cold hydrochloric acid  $73.8^\circ$ , inversion by invertase  $74.0^\circ$ . These results show that the acid methods indicate more cane sugar than does the invertase hydrolysis and there is no question but that the invertase determination is more nearly correct.

*The Hydrolysis of Raffinose by Invertase.*—The peculiar trisaccharide raffinose, which occurs in cotton seed, in wheat, and in the sugar beet, is hydrolyzed by invertase, and the method for estimating cane sugar by inversion with invertase is accordingly not applicable in case raffinose is present. Raffinose is also hydrolyzed by hydrochloric acid, and therefore the acid hydrolysis has here no advantage over that by invertase. An experiment was performed in which a 10 per cent. solution of very pure recrystallized raffinose, of specific rotation  $123^\circ$  (circular), was hydrolyzed with the stock invertase solution, and the rotation was found to change to  $67.6^\circ$  at  $20^\circ$ , where it remained constant.

*The Action of Invertase on Other Acid-hydrolyzable Substances.*—The stock solution of invertase has been found to be entirely incapable of hydrolyzing lactose, maltose, starch, dextrin, cellulose, pentosans, amygdalin or salicin. So far no action on any substances except cane sugar and raffinose has been detected, but it appears probable that the tetrasaccharide stachyose, which occurs in some plants, would be split into fructose and a trisaccharide.

*Summary.*—The enzyme invertase accomplishes a complete inversion of cane sugar and is without action on starch, dextrin, maltose, lactose, pentosans and natural glucosides. A procedure for preparing

stock solutions of invertase from pressed yeast has been worked out and the solutions found to be permanent in inverting power, the measurements having been made now for a period of fifteen months. The invertase inverts only in an acid medium and the best acid to use is found to be acetic. Full directions for the method of analysis are given and the possible errors due to the slight rotatory power of the invertase solution and the mutarotation of the invert sugar are investigated and means taken to avoid them. The formula for the percentage of cane sugar is found to be

$$\frac{(S - I)}{141.7 - T} \times 100, \text{ where } S \text{ and } I \text{ are}$$

the direct and invert readings of the solution, T the temperature and 141.7 the inversion constant, which differs from that for the inversion by hydrochloric acid, *i. e.*, 142.7. This difference is shown to be due to the influence of the acidity on the rotation of invert sugar, as the hydrochloric acid solutions give after neutralization the invertase constant 141.7. It is found that raffinose is hydrolyzed by invertase and that its specific rotation is thereby reduced from  $123^\circ$  to  $67.6^\circ$ ; raffinose accordingly interferes with the estimation of cane sugar by the use of invertase, just as it also interferes when the inversion is carried out with hydrochloric acid. Analyses of cane sugar in pure cane sugar, Louisiana molasses, and bagasse by the invertase method of hydrolysis give percentages which agree with those obtained by the hydrochloric acid hydrolysis. The Sotol plant (*Dasylirion texanum*) is shown to contain only a trace of cane sugar, but 13 per cent. of an unknown carbohydrate which is being further investigated.

## BACTERIOLOGICAL METHODS FOR DETERMINING THE AVAILABLE NITROGEN IN FERTILIZERS.

By JACOB G. LIPMAN.

Received February 17, 1910.

Attempts to determine the relative availability of nitrogenous fertilizers by measuring the amounts of nitrate formed from them under definite experimental conditions have been made by different investigators. In consequence of these investigations it is now well known that nitrate formation from organic substances bears a direct relation to the proportion of nitrogen contained in them, and in general, to the ease with which they will undergo decomposition. A much larger amount of work on the same subject has been done from the crop standpoint; that is, the relative availability of nitrogenous substances has been determined not by measuring the quantity of nitrate formed from them under definite experimental conditions, but by measuring the amounts of nitrogen furnished by each to the crop, as shown by analyses of the latter.

<sup>1</sup> J. Amer. Chem. Soc., 17, 312 20 (1895).

In view of the fact that nitrate formation from organic substances is preceded by ammonia formation, it is proper to assume that nitrification is more or less directly affected by ammonification. Substances that will ammonify readily should also nitrify readily, and *vice versa*. Nevertheless, it is theoretically possible that the relative ammonification of a group of nitrogenous substances need not correspond exactly to their relative nitrification. It, therefore, appeared advisable to make a series of tests on the relative ammonification and nitrification of a number of such substances. It was hoped, also, that among other things these tests would give some indication as to the practicability of measuring the relative availability of nitrogenous materials by their ammonification, as well as their nitrification. It is to be added here, that the experiments recorded below are hardly more than preliminary, and will be continued in the future.

The nitrogenous materials in these tests were mixed in each case with 100 grams of soil and 1 gram of calcium carbonate. The soils themselves were kept at their optimum moisture content, *viz.*, 18 per cent. In the ammonification tests additional amounts of water were supplied so as to provide in each case organic matter containing 75 per cent. of water. For instance, when 5 grams of dried blood were employed there were added 15 cc. of water aside from that added to the soil itself; when approximately 30 grams of dried manure were used the amount of water added was about 90 cc., etc. Thanks to this method it was possible to maintain uniform moisture conditions in the several soil portions. Both in the nitrification and ammonification tests the materials were added so as to supply equal amounts of nitrogen. The nitrogen content of the different substances was as follows:

	Per cent.
Ammonium sulphate.....	20.30
Calcium cyanamid.....	17.64
Dried blood.....	10.76
Concentrated tankage.....	12.63
Ground fish.....	7.90
Cottonseed meal.....	6.40
Bone meal.....	1.35
Solid and liquid manure, fresh.....	3.07
Solid manure, fresh.....	2.20
Solid and liquid manure, leached.....	1.72
Horse manure.....	1.31

Ammonia determinations were made at the end of six days, and nitrate determinations at the end of four weeks in the corresponding series. The amounts of material used and those of ammonia and nitrate nitrogen found were as follows:

As is shown in the table below considerable quantities of nitrogen were split off either in the form of ammonia or of nitrate. Small quantities of nitrites were also found in the nitrification series, yet they were quite uniform, and so insignificant in amount as to make it unnecessary to record them here. The proportion of the amounts of nitrogen found as am-

Soil portion No.	Additions.	Ammonia N		Aver.
		found.	Mgs.	
1	5 grams dried blood.....	91.51		
2	5 grams dried blood.....	88.67		90.09
3	4.26 grams concentrated tankage.....	312.95		
4	4.26 grams concentrated tankage.....	297.99		305.47
5	6.81 grams ground fish.....	247.43		
6	6.81 grams ground fish.....	260.03		253.73
7	8.41 grams cotton-seed meal.....	32.13		
8	8.41 grams cotton-seed meal.....	21.42		26.77
9	39.85 grams bone-meal.....	78.43		
10	39.85 grams bone-meal.....	102.06		90.24
11	17.52 grams solid and liquid manure, fresh.....	180.49		
12	17.52 grams solid and liquid manure, fresh.....	170.41		175.45
13	24.45 grams solid manure, fresh.....	28.19		
14	24.45 grams solid manure, fresh.....	29.77		28.98
15	31.28 grams solid and liquid manure, leached.....	62.37		
16	31.28 grams solid and liquid manure, leached.....	62.37		62.37
17	29.72 grams horse manure.....	40.00		
18	29.72 grams horse manure.....	36.85		38.42

Soil portion No.	Additions.	Nitrate N		Increase over the untreated portions.	
		found.	Aver.	Mgs.	Mgs.
1	0.....	5.332			
2	0.....	5.332	5.33		
3	100 mgs. ammon. sulphate.....	21.332			
4	100 mgs. ammon. sulphate.....	20.720	21.26		15.928
5	115 mgs. calcium cyanamid.....	5.481			
6	115 mgs. calcium cyanamid.....	16.00	16.00		10.668
7	189 mgs. dried blood.....	10.56			
8	189 mgs. dried blood.....	10.71	10.63		4.298
9	161 mgs. concentrated tankage.....	16.21			
10	161 mgs. concentrated tankage.....	16.19	16.20		10.868
11	257 mgs. ground fish.....	10.75			
12	257 mgs. ground fish.....	10.53	10.64		5.318
13	317 mgs. cotton seed meal.....	10.46			
14	317 mgs. cotton seed meal.....	12.65	11.55		6.218
15	1504 mgs. bone-meal.....	7.74			
16	1504 mgs. bone-meal.....	7.92	7.83		2.498
17	661 mgs. solid and liquid manure, fresh.....	7.80			
18	661 mgs. solid and liquid manure, fresh.....	8.00	7.90		2.568
19	923 mgs. solid manure, fresh.....	7.22			
20	923 mgs. solid manure, fresh.....	7.29	7.25		1.118
21	1180 mgs. solid and liquid, leached.....	6.16			
22	1180 mgs. solid and liquid, leached.....	6.32	6.24		0.908
23	1122 mgs. horse manure.....	7.08			
24	1122 mgs. horse manure.....	7.14	7.11		1.778

monia or nitrate, to the amounts applied may serve as an indication of the relative availability of the different materials. These proportions, designated as nitrogen recovered, are shown in the following table:

	PER CENT. OF NITROGEN RECOVERED	
	Ammonifica- tion series.	Nitrifica- tion series.
Ammonium sulphate.....	...	78.47
Calcium cyanamid.....	...	52.56
Dried blood.....	16.74	26.13
Concentrated tankage.....	56.66	53.54
Ground fish.....	47.16	26.15
Cottonseed meal.....	4.95	30.64
Bone meal.....	16.65	12.31
Cow manure, solid and liquid fresh.....	32.60	12.67
Cow manure, solid fresh.....	5.39	9.46
Cow manure, solid and liquid leached.....	11.59	4.48
Horse manure.....	7.14	8.76

In comparing the figures before us we should remember that ammonia was determined at the end of six days and nitrate at the end of four weeks. There is no doubt that two or three days more would have not only increased the amounts of ammonia produced in the ammonification series, but would have modified to some extent the relative recovery. It is also true

<sup>1</sup> Not included in the average.

that another week or two in the nitrification series would have resulted in slight modifications in the relative availability of the different materials as measured by nitrate production. For all that the results are of considerable interest even as they are. We note, for instance, that concentrated tankage, ground fish, solid and liquid manure fresh, dried blood and bone meal in the order given yielded the largest amounts of ammonia; and concentrated tankage, cotton-seed meal, ground fish, dried blood and solid and liquid manure, fresh, in the order given yielded the largest amounts of nitrate. Concentrated tankage heads the list, in each case, while three others are also found in each group. The surmise, therefore, that easily ammonifiable substances are also easily nitrifiable is borne out by the present data. Nevertheless there are some discrepancies that are of considerable moment. It will be observed that next to concentrated tankage, cotton-seed meal proved the most easily nitrifiable of the organic materials. In the ammonification series, on the other hand, cotton-seed meal was found to possess a low rate of availability. In view of other experiments carried out by us, showing the depressing effect of soluble carbohydrates on ammonification, the low rate of availability of cotton-seed meal in the ammonification series is not without interest.

In comparing further the relative availabilities of the same materials in the ammonification and nitrification series it should be remembered that small quantities of material are transformed more thoroughly and more efficiently in the soil than larger quantities. Hence, the relations in the two series are somewhat different in this respect. It is also likely that in different soils the relations found in the two series would be modified. With that much admitted, however, it is instructive to note how rapidly some substances may be broken down by bacteria. We find, for instance, that in the ammonification series 56.65 per cent. of the nitrogen contained in the concentrated tankage was changed to ammonia in six days. Similarly, 47.16 per cent. and 32.60 per cent. in the ground fish and the solid and liquid manure, fresh, respectively were transformed into ammonia. On the contrary, the three other samples of manure proved to have a low rate of availability, both in the ammonification and nitrification series. It should be noted, here however, that the samples of manure employed in the present experiments had been previously dried on the water bath and kept in a dry state for some time. Naturally, the drying reduces the availability of nitrogenous materials, hence the returns, as noted above, are smaller than they would have been had the manure in question been used in a fresh condition. It may be of interest to cite here the results secured with similar samples of manure in our cylinder experiments extending over a period of ten years. It was

found in these experiments<sup>1</sup> that solid manure, fresh; solid and liquid, fresh; and solid and liquid, leached gave recoveries of 22.31 per cent., 32.91 per cent. and 26.75 per cent., respectively, in a ten-year period, in which two rotations of corn, oats, wheat and grass had been completed. The manure was applied annually and the figures given above represent, therefore, the cumulative effect of the manure residue. In single seasons much lower returns have been secured in a number of instances. Thus the corresponding recoveries in the corn crop of 1908 were<sup>2</sup> 11.20 per cent., 17.55 per cent. and 11.50 per cent., respectively. On the whole, it is not unlikely that the methods outlined above will prove very convenient not only for measuring the relative availability of nitrogenous fertilizers, but also for determining the availability of the nitrogen in humus derived from different soils.

### ACCURACY IN TAKING AND PREPARING MIXED FERTILIZER SAMPLES.

By F. B. PORTER

The importance of accuracy in taking and preparing samples of fertilizer material is often well understood by those having charge of such work. It does not, however, always follow that the sample analyzed in the laboratory is a correct one.

The following tables, I and II, give an idea of the lack of agreement in analyses of mixed fertilizers.

Table I gives differences in analyses on samples put up in pint jars by this laboratory and sent to the laboratory "A" after taking out a four-ounce bottle sample without previous grinding.

Table II gives differences in analyses on the same shipment of goods, sampled and analyzed before shipment at this plant and at destination by the State to which it was sent. All of the above materials passed a 3-mesh screen before sampling. Samples in Table II were taken at this plant with a three-foot trier from at least 10 per cent. of the bags giving a sample weighing one pound, or over. This was quartered down to about 85 grams and then ground to pass a 20-mesh screen. Most State inspectors take their samples in the same general way and it is doubtful if any reduce the size of the particles in the one-pound samples before quartering as the work here reported indicates should be done. The above tables show greater discrepancy than can be accounted for by laboratory errors and it will be noted by comparing the two, that the differences increase where the sampling is by different parties, as in the case of Table II.

A glance at the various official methods for sampling will help very little in reducing these differences, in fact, none of them give complete and definite directions for sample preparation. The official directions of the

<sup>1</sup> Bull. 221, N. J. Exper. Station, p. 23.

<sup>2</sup> Voorhees and Lipman, "Experiments on the Utilization of Nitrogen in Fertilizer Materials," THIS JOURNAL, 1, 397 (1909).



A. O. A. C. simply require the fertilizer to pass a sieve with 1 mm. diameter perforation.<sup>1</sup> The official directions of the International Congress of Applied Chemistry only specify the number of packages or buckets to be sampled, require crushing to size of a hazel-nut and require the sample sent to laboratory to weigh 300 grams.<sup>2</sup> The method of the French Experiment Station merely requires the reduction to a coarse powder before

general principles upon which to base such judgment. An occasional double sampling of the same lot of goods has been the only foundation for some of the sampling systems in use. The prevalent general idea has been that the larger the sample and the smaller the individual pieces in it, the more accurate it would be. Mr. Bailey has put this into a more definite form originating the new term "Size-Weight-Per Cent.," and

TABLE I.—ANALYSES MADE ON SAME PINT JAR SAMPLE BY DIFFERENT LABORATORIES—SEASON 1908-1909.

Brands, Laboratory.	Total phos. acid.			Avail. phos. acid.			Ammonia.			Potash.		
	A	B.	Diff.	A.	B.	Diff.	A.	B.	Diff.	A.	B.	Diff.
9-3-2.....	11.72	11.80	0.08	9.21	9.82	0.61	3.02	3.07	0.05	2.46	2.58	0.12
9-2-1.....	11.69	11.43	0.26	9.85	9.83	0.02	2.10	2.18	0.08	1.48	1.48	0.00
10-2-2.....	12.79	12.30	0.49	10.79	10.45	0.34	2.10	2.23	0.13	2.48	2.58	0.10
10-0-4.....	12.14	12.10	0.04	10.59	10.95	0.36	.....	.....	.....	4.43	4.64	0.21
10-0-2.....	12.14	12.45	0.31	10.26	11.12	0.86	.....	.....	.....	2.39	2.56	0.17
8-2-2.....	10.40	10.25	0.15	8.57	8.55	0.02	2.21	2.18	0.03	2.13	2.42	0.29
8-4-4.....	11.49	11.18	0.31	8.83	8.13	0.70	4.02	4.20	0.18	5.51	4.50	1.01
8-2-2.....	10.34	10.25	0.09	8.43	8.55	0.12	2.21	2.18	0.03	2.05	2.42	0.37
Average difference,			0.22			0.38			0.08			0.28
SEASON 1907-1908.												
9-3-2.....	11.82	11.65	0.17	9.21	9.05	0.16	3.35	3.50	0.15	2.15	2.32	0.17
9-2-1.....	11.62	11.65	0.03	9.46	9.62	0.16	2.46	2.28	0.18	1.25	1.06	0.19
10-2-2.....	12.59	12.30	0.29	10.61	10.05	0.56	2.56	2.43	0.13	2.12	2.40	0.28
10-0-4.....	11.73	11.78	0.05	10.60	10.58	0.02	.....	.....	.....	3.92	4.10	0.18
10-0-2.....	11.85	12.05	0.20	10.48	10.90	0.42	.....	.....	.....	1.89	2.38	0.49
8-2-2.....	10.51	10.00	0.51	8.62	8.15	0.47	2.30	2.01	0.29	2.16	2.72	0.56
8-4-4.....	11.28	11.10	0.18	8.02	8.15	0.13	4.04	4.26	0.22	4.65	4.44	0.21
8-2-2.....	10.53	10.00	0.53	8.71	8.15	0.56	2.26	2.01	0.25	2.20	2.72	0.52
Average difference,			0.24			0.31			0.20			0.32

mixing and taking the final sample.<sup>3</sup> The International Commission merely requires mixing and attention to moisture changes.<sup>4</sup> The German method requires the sample to weigh 2 kg. and to be sifted if possible, and mixed.<sup>5</sup> There is very little in any of the above that is of value in judging the accuracy of sampling

for coal given figures which will enable any one to take and prepare a sample on which the error in ash determination will not be more than 1 per cent.

The attempt in this paper will be to give similar figures for use in sampling commercial fertilizer. In the case of fertilizer there are as high as three constitu-

TABLE II.—ANALYSES ON SAME SHIPMENT-SAMPLING AND ANALYSIS BY DIFFERENT PARTIES.

Lab. No.	Brand.	Laboratory.	Total phos. acid.			Avail. phos. acid.			Ammonia.			Potash.		
			A	C D	B.	A	C D	B.	A	C D	B.	A	C D	B.
1258	8-2-2	C	9.60	10.18	0.58	9.22	9.75	0.53	2.36	2.24	0.12	2.75	2.08	0.63
1259	8-2-2	C	8.70	9.45	0.75	8.25	9.07	0.82	2.71	2.50	0.21	2.26	1.91	0.35
1260	8-2-2	C	9.35	8.95	0.40	8.66	8.55	0.11	2.18	2.50	0.32	1.50	1.17	0.37
1261	9-2-1	C	9.00	9.90	0.90	8.57	9.32	0.75	2.45	2.34	0.11	1.60	1.03	0.57
418	9-2-1	C	9.65	10.75	1.10	9.11	10.02	0.91	1.75	1.92	0.17	2.11	1.42	0.69
728	10-0-4	D	.....	.....	.....	9.32	9.90	0.58	.....	.....	.....	3.02	2.22	0.80
584	8.75-2-2	D	10.28	9.58	0.70	9.81	8.95	0.86	2.30	2.43	0.13	1.40	1.67	0.27
585	10-0-2	D	11.02	10.93	0.09	10.66	10.35	0.31	.....	.....	.....	1.62	2.01	0.39
1422	8-4-4	A	10.94	10.73	0.21	9.17	9.38	0.21	3.13	3.62	0.49	2.86	4.14	1.28
1423	8-2-2	A	10.13	9.05	1.08	9.75	8.52	1.23	1.42	1.86	0.44	1.50	1.93	0.43
8.87	13-0-4	E	.....	.....	.....	11.75	13.20	1.45	.....	.....	.....	4.03	3.51	0.52
1068	10-2-2	E	.....	.....	.....	10.80	10.30	0.50	1.86	1.74	0.12	1.52	1.39	0.13
1256	9-3-2	E	.....	.....	.....	9.50	8.43	1.07	2.83	2.99	0.16	1.34	1.46	0.12
Average difference,					0.65			0.78			0.25			0.54

and sample preparation. As Dr. Wiley says, the matter of correct sampling is left principally to the judgment of the one in charge.<sup>6</sup>

Mr. Bailey's article on "Accuracy in Sampling Coal"<sup>7</sup> was practically the first attempt to set forth

ents on each of which the money consideration on 1 per cent. in a ton is over 10 times as great as in the case of ash in coal. The fact that goods are pulverized to pass a 2- to 5-mesh screen before shipping makes the sampling less difficult but does not make it as easy as has been supposed. The laboratory limit of error is necessarily quite high, making it difficult to determine where its effect stops and where the sampling error begins.

To determine whether the size-weight-per cent. is the controlling factor in fertilizer sampling and to

<sup>1</sup> Bureau of Chem., U. S. Dept. of Agr., Bulletin 107, p. 1.

<sup>2</sup> Wiley's "Principles and Practice of Agricultural Analysis," Vol. 2, p. 16, 2d Edition.

<sup>3</sup> *Ibid.*, p. 17.

<sup>4</sup> *Ibid.*, p. 20.

<sup>5</sup> *Ibid.*, p. 21.

<sup>6</sup> *Ibid.*, p. 17.

<sup>7</sup> THIS JOURNAL, 1, 163.

obtain figures that will enable us to sample any lot of fertilizer with a known degree of accuracy, the following experimental work was undertaken: A mixture was made of

5 lbs	51% muriate potash
25 "	16% acid phosphate
20 "	10 5% tankage

All of these materials had passed a 3-mesh screen and had been rejected on a  $4\frac{1}{2}$ -mesh screen. This

remaining part of the 25-pound sample was quartered to 150 grams 10 times and these 10 samples combined and ground to pass a 20-mesh sieve. It was found that the lighter materials in this sample separated out, as sometimes happens in fertilizers, so one-half of it was ground to pass an 80-mesh sieve and this latter sample was used to determine the correct analysis of the original 50 pounds. The analyses of the 20-

TABLE III.—RESULTS OF AMMONIA DETERMINATIONS.

Average weight of sample gms.	Composite.	Composite	74.4	36	84.2	17.8	35.2	18.2	105.9	50.6	24.7
Wt. largest particle in grams	0.0000047	0.00034	0.0067	0.0067	0.250	0.0067	0.250	0.250	0.2764	0.2764	0.2764
Sieve through which passed			8m.	8m.	$4\frac{1}{2}$ m.	8m.	$4\frac{1}{2}$ m.	$4\frac{1}{2}$ m.	3m.	3m.	3m.
"Size-weight-per cent"	0.00012	0.0085	0.0045	0.0093	0.0143	0.0188	0.355	0.068	0.131	0.273	0.56
Ground to pass	80m.	20m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.
4.42	4.48	4.52	4.61	4.65	4.35	4.84	4.80	4.46	4.65	4.29	4.29
4.46	4.27	4.44	4.50	4.26	4.58	4.63	4.63	4.76	4.26	4.84	4.84
4.40	4.27	4.41	4.56	4.39	4.61	4.37	4.48	4.32	4.18	4.86	4.86
4.37	4.31	4.41	4.50	4.44	4.84	4.48	4.44	4.00	4.73	4.76	4.76
4.44	4.27	4.35	4.46	4.52	4.54	4.63	4.22	4.13	4.18	4.56	4.56
4.42	4.54	.....	.....	.....	.....	.....	.....	4.35	4.12	4.50	4.50
4.46	3.90	.....	.....	.....	.....	.....	.....	4.15	4.12	4.23	4.23
4.44	4.16	.....	.....	.....	.....	.....	.....	4.15	4.24	3.97	3.97
4.42	4.35	.....	.....	.....	.....	.....	.....	4.53	4.78	4.29	4.29
4.48	4.31	.....	.....	.....	.....	.....	.....	4.24	4.65	4.18	4.18
Average	4.34	4.29	4.43	4.52	4.46	4.58	4.59	4.51	4.31	4.39	4.45
Maximum error from 4.43	0.06	0.39	0.09	0.09	0.20	0.41	0.41	0.37	0.43	0.35	0.46
Error of average from 4.43	0.00	0.14	0.00	0.18	0.03	0.15	0.16	0.08	0.12	0.04	0.02
Probable error calc.	0.02	0.155	0.042	0.083	0.099	0.166	0.173	0.159	0.175	0.187	0.228
Possible error calc.	0.123	0.886	0.238	0.470	0.565	0.943	0.966	0.910	0.996	1.065	1.17

makes an extreme case on all three ingredients, which would seldom if ever occur in practice, but which does often obtain to a large extent on one or more ingredients. The above mixture was quartered once and one-half set aside as a reserve portion. The other half was quartered down to about 100 grams and this placed in a bottle. The second half from the last quartering was quartered and a 50-gram sample saved; likewise a 25-gram sample was obtained and the remaining 25 grams returned to the original.

mesh portions have been included in the tables as an illustration of other factors which may influence the results.

In the following tables the probable and possible errors are calculated from the following formulas:

$$\text{Probable error} = 0.6745 \sqrt{\frac{\sum e^2}{N-1}}$$

$$\text{Possible error} = 3.84 \sqrt{\frac{\sum e^2}{N-1}}$$

TABLE IV.—RESULTS OF TOTAL PHOSPHORIC ACID DETERMINATIONS.

Average wt. sample grams	Composite.	Composite.	74.4	36	84.2	17.8	35.2	18.2	105.9	50.6	24.7
Wt. largest particle in grams	0.00001	0.008	0.028	0.0128	0.040	0.0128	0.40	0.040	0.4607	0.4607	0.4607
Sieve through which passed			8m.	8m.	$4\frac{1}{2}$ m.	8m.	$4\frac{1}{2}$ m.	$4\frac{1}{2}$ m.	3m.	3m.	3m.
"Size-weight-per cent"	0.00025	0.020	0.0086	0.1780	0.0237	0.035	0.055	0.11	0.217	0.455	0.935
Ground to pass	80m.	20m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.
12.80	12.68	12.45	12.58	12.50	12.78	12.30	12.20	12.70	12.63	12.45	12.45
12.65	12.78	12.65	12.58	12.60	12.83	12.38	12.30	12.55	12.85	12.35	12.35
12.63	12.80	12.50	12.65	12.40	12.68	12.40	12.28	12.08	12.30	12.35	12.35
12.78	12.70	12.43	12.68	12.53	12.65	12.58	12.60	11.98	11.75	11.98	11.98
12.60	12.73	12.68	12.70	12.53	12.80	12.85	12.75	12.45	12.40	11.93	11.93
12.55	12.64	12.85	.....	12.85	12.72	.....	.....	12.50	13.05	12.68	12.68
12.65	12.63	12.83	.....	12.65	13.06	.....	.....	12.15	12.75	12.45	12.45
12.70	12.75	12.75	.....	12.68	12.78	.....	.....	12.33	12.45	12.45	12.45
12.63	12.68	12.75	.....	12.75	12.76	.....	.....	12.00	12.73	11.93	11.93
12.63	12.78	12.80	.....	12.90	13.04	.....	.....	12.50	11.85	12.13	12.13
Average	12.66	12.71	12.67	12.63	12.64	12.81	12.50	12.43	12.32	12.48	12.30
Maximum error from 12.66	0.14	0.14	0.23	0.08	0.26	0.40	0.36	0.46	0.66	0.91	1.73
Error of average from 12.66	0.00	0.05	0.01	0.03	0.02	0.15	0.16	0.23	0.34	0.18	0.36
Probable error calc.	0.0523	0.0573	0.1063	0.041	0.1083	0.149	0.190	0.2380	0.294	0.312	0.326
Possible error calc.	0.298	0.326	0.408	0.234	0.417	0.850	1.082	1.355	1.676	1.780	1.858

This process was repeated 10 times, giving 30 samples. The remainder of the original 25 pounds was then crushed to pass a  $4\frac{1}{2}$ -mesh screen and the same process carried out five times, giving 15 samples. The large sample was again crushed and passed through an 8 mesh screen and quartered down five times as before, making a total of 60 samples. The

in which  $\sum e^2$  equals the sum of the squares of the individual errors and N is the number of tests from which the errors are taken.

To determine the sizes of the particles used in these tables, curves were located by plotting the mean of the linear dimensions of the opening in two screens and the weights of the average particle rejected by

one screen and passed by the other of these same screens. Then from these curves the weight of the largest particle passing any screen was read off, using the side of the opening in the given screen. The size-weight-per cent. was calculated as follows: Size-weight-per cent. =  $\frac{\text{weight of largest particle} \times 100}{2 \times \text{weight of sample}}$

Omitting the 20-mesh composite sample, the in-

enough toward the origin of the curve to give us, with reasonable accuracy, the point S on curve No. 2, sheet 1, which will be used later. It is likely that a larger number of samples would have brought all the points much nearer the curve.

In the case of potash, the irregularities were of more serious character, the average being below in several cases. Two possible reasons for this were

TABLE V.—RESULTS OF POTASH DETERMINATIONS.

Average wt. sample grams.....	Composite.	Composite.	74.4	36	84.2	17.8	35.2	18.2	105.9	50.6	24.7
Wt. largest particle in grams.....	0.00001	0.0008	0.0121	0.0121	0.029	0.0121	0.029	0.029	0.2937	0.2937	0.2937
Sieve through which passed.....			8m.	8m.	4 1/2 m.	8m.	4 1/2 m.	4 1/2 m.	3m.	3m.	3m.
"Size-weight-per cent.".....	0.00005	0.004	0.0082	0.0168	0.172	0.034	0.0412	0.079	0.138	0.290	0.595
Ground to pass.....	80m.	20m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.	80m.
	4.42	4.23	4.59	4.56	4.11	4.40	4.56	3.96	4.27	4.24	5.88
	4.48	4.35	4.49	4.65	3.91	4.21	4.62	4.29	4.18	3.74	3.65
	4.53	4.38	4.49	4.35	4.42	4.57	4.87	4.63	4.46	4.22	3.87
	4.66	4.37	4.68	4.51	4.31	5.15	4.32	4.09	5.28	4.76	5.03
	4.56	4.25	4.41	4.41	4.27	4.19	4.08	4.43	4.70	4.71	5.40
	4.30	4.21	.....	.....	.....	.....	.....	.....	4.33	4.19	3.14
	4.59	4.30	.....	.....	.....	.....	.....	.....	4.87	5.11	5.07
	4.37	4.34	.....	.....	.....	.....	.....	.....	4.92	4.58	4.97
	4.47	4.25	.....	.....	.....	.....	.....	.....	4.67	4.80	4.96
	4.32	4.41	.....	.....	.....	.....	.....	.....	4.05	4.54	4.74
Average.....	4.47	4.32	4.59	4.49	4.20	4.50	4.49	4.28	4.57	4.49	4.67
Maximum error from 4.47.....	0.19	0.26	0.21	0.18	0.56	0.68	0.40	0.51	0.81	0.73	1.41
Error of aver. from 4.47.....	0.00	0.15	0.12	0.02	0.27	0.03	0.02	0.19	0.10	0.02	0.20
Probable error calc.....	0.08	0.124	0.085	0.08	.....	0.266	0.20	0.22	0.27	0.27	0.59
Possible error calc.....	0.45	0.706	0.482	0.47	1.59	1.51	1.16	1.25	1.53	1.52	3.36

redients of which separated in the bottle as noted above, there are but two of the possible error figures which do not fall on the curve No. 1, sheet 1. These figures would probably fall on the curve had they been calculated from ten or twenty determinations instead of five.

In addition to figures in Table IV on total phosphoric acid, the possible error was also calculated for avail-

suggested. Either that the moisture from the acid phosphate and air dissolved potash from the crystals and this solution was lost on the sampling cloth, or that in some sets of samples the potash was "retained"<sup>1</sup> more than in others.

A second set of samples was therefore made up using dry, fine sand in place of the tankage and acid phosphate used above, care being taken not to handle these

TABLE VI.—RESULTS ON POTASH IN SAND MIXTURE.

Average wt. sample grams.....		86.7	41.5	84.7	21.2	40.2	20.5	98.1	48	23.4
Wt. largest particle in grams.....	0.00001	0.0121	0.0121	0.029	0.0121	0.029	0.029	0.2937	0.2937	0.2937
Sieve through which passed.....		8m	8m.	4 1/2 m.	3m.	4 1/2 m.	4 1/2 m.	3m	3m.	3m.
"Size-weight-per cent.".....		0.0070	0.146	0.171	0.0286	0.0365	0.0707	0.149	0.306	0.626
Ground to pass.....	60m.	60m.	60m.	60m.	60m.	60m.	60m.	60m.	60m.	60m.
1	5.18	4.92	5.09	4.39	4.74	6.53	4.66	3.83	4.35	7.75
2	5.31	5.31	4.77	4.16	4.73	4.06	4.72	3.14	3.92	5.26
3	5.21	5.65	6.04	4.46	7.09	5.18	4.61	4.13	5.66	5.15
4	5.35	5.16	4.93	4.69	4.84	5.47	4.61	4.84	4.86	3.58
5	5.39	5.59	5.98	4.59	6.85	4.94	4.87	4.26	4.55	7.57
6	5.33	5.12	5.92	5.25	4.67	4.49	5.57	4.78	5.07	4.82
7	5.35	5.18	5.47	5.13	5.44	5.28	5.30	4.88	6.00	5.67
8	5.33	5.55	6.29	4.89	5.42	5.88	3.56	3.69	4.99	6.32
9	5.38	5.31	6.10	5.24	5.71	5.96	4.57	4.64	4.56	3.49
10	5.37	4.83	5.14	4.97	5.16	5.31	6.14	3.69	4.87	5.56
Average.....	5.32	5.27	5.57	4.78	5.22	5.31	4.86	4.19	4.88	5.52
Maximum error from.....	5.32	0.00	0.49	0.97	1.16	1.77	1.26	1.76	2.18	1.40
Error of average from.....	5.32	0.14	0.05	0.25	0.54	0.10	0.01	0.46	Spilled by	0.44
Probable error.....	0.047	0.047	0.191	0.416	0.462	0.594	0.484	0.559	mechanical	0.507
Possible error.....	0.23	0.045	2.06	2.28	2.94	2.40	2.77	losses.	2.53	5.54

able, but owing to the introduction of the second laboratory error in the insoluble, the results were not uniform.

Considerable irregularity of results was found on total phosphoric acid at first, but on making up three second sets of samples from the reserve 25 pounds, the possible error figures became uniform down far

samples when the relative humidity in the room was above 75%. Following are the results on this test.

It was found that, while this avoided the difficulties above mentioned, it was very difficult to grind and sift these samples without loss into the air, of very fine particles of potash. Because of inattention to

<sup>1</sup> THIS JOURNAL, May, 1909.



this detail, the results on the 3-mesh 100-gram samples were made useless and have been omitted from the curve. The possible errors in the last set of figures, Table VI, are much higher than on the fertilizer, Table V. If, however, by simple proportion, a calculation is made as to what error to expect from the concentration of the materials used, using the ammonia results as the basis, the results from the sand sample will be found to agree closely with the calculated figures. The following table illustrates this point, all the figures being on the 3-mesh 25-gram samples.

TABLE VII

Material used.	Concentration of ingredients tested for	Possible error found.	Possible error calculated from the ammonia figure.
Tankage.	10 5 per cent. ammonia	1.17	....
Acid phosphate.	17 0 per cent. tot. phos. acid	1.86	1.89
Mur. pot. in fert.	51 0 per cent. potash	3.86	5.69
Mur. pot. in sand.	51 0 per cent. potash	5.54	

The writer believes that the low possible errors in potash on fertilizers are due to the solution of potash in the acid phosphate and tankage moisture, making it not a case of sampling a mixture of 51 per cent. crystals, acid phosphate and tankage, but rather mixture of crystals reduced in size by solution and acid phosphate and tankage carrying potash dissolved in their moisture contents.

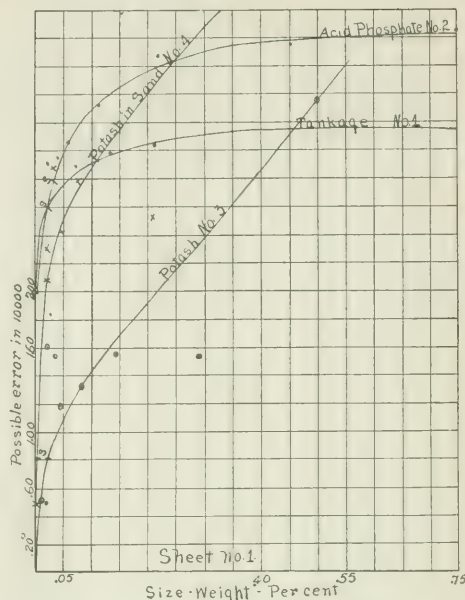
Such action as this would not be likely to go on to the same extent in each of the 60 samples above and would possibly account for some of the irregularities in the results obtained on potash in the fertilizer. It has been evident throughout the work, however, that a large part of the irregularities disappear as the number of samples is increased.

The above results can be put into a more convenient and practical form by deciding what possible and probable error can rightly be allowed to the process of sampling and then determine the weight of sample necessary from any sieve to give that result. It is desirable to restrict the possible error due to sampling to 0.50 per cent. with the corresponding probable error of 0.088 per cent. This added to the possible error found on the 80 m. composite sample which we have taken as the laboratory limit gives the following figures. An average of the two laboratory limit figures has been taken on the potash work.

TABLE VIII.

	Allowable possible error. Per cent.	Corresponding size-weight-per cent.
Tankage (ammonia)	0.633	0.02
Acid phosphate (phos. acid)	0.80	0.03
Muriate of pot. in fert. (potash)	0.80	0.03
Muriate of pot. in sand (potash)	0.80	0.005

These possible error figures give the points on the curves, sheet 1, marked S and from them the corresponding size-weight-per cents. given above were read off. Calculating the weight of sample for the different



mesh screens, using these size-weight-per cents. and the weight of the largest particles for the screens, we have:

TABLE IX.  
Grams of fertilizer sample necessary to give 0.50 per cent. sampling possible error.

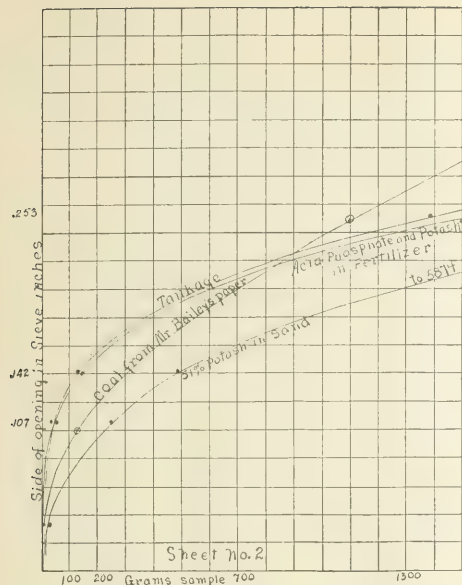
Size of opening in screen.	Mesh of screen.	On ammonia.	On potash and phos. acid in fert.	On potash in sand.
0.253	3	1382	1535	5874
0.142	4.5	125	133	580
0.107	8	34	43	242
0.033	20	1.13	2.56	13
0.170	4	290	310	800

Plotting these grams of samples and dimensions of openings in screens gives the curves on sheet No. 2 from which the weight of sample for any screen can be determined if the dimensions of openings in the screen are known. In this way, the above figures for 4-mesh screen were obtained.

The taking and preparing larger samples of course means more work. In view of this fact, it does not seem advisable to take samples as large as indicated by the potash and sand results, Table VI, except perhaps in special cases. This is especially true until such a time as such figures as are given in Table VI have been obtained on commercial fertilizer mixtures.

In conclusion, the following points are noted:

1. Discrepancies in the analyses of the same shipment are much greater than they should be.
2. Discrepancies are largely due to sampling as shown by a comparison of averages on Tables I and II and as shown by the errors from the averages on Tables III, IV, and V.



3. Possible error increases with the size-weight-per cent., giving a fairly uniform curve. Irregularities are the greatest in case of potash.

4. The possible error seems to increase in simple proportion with the percentage of the ingredient analyzed for in the material used to furnish that ingredient, provided there is not some factor which modifies this.

5. For a chosen degree of sampling accuracy the weight of sample required on goods from any known mesh or screen can be determined.

6. For a possible sampling error of 0.50 per cent. on fertilizer from a 3-mesh screen, a sample weighing 1535 grams ( $3\frac{1}{2}$  pounds) should be taken and passed through a finer mesh sieve before quartering. Subsequent handling should be kept within the bounds indicated by sheet 2 and Table IX. These are the points at which most present fertilizer sampling systems are weak.

7. Strict adherence to the above suggestions will not obviate the difficulties due to imperfectly mixed goods, but given well-mixed goods and inspectors who will correctly take and prepare samples as indicated by the size-weight-per cent. figures given, the writer is confident that the wide variations so common to-day will disappear.

This work has been done under certain limitations, especially as to time, and it is hoped that some one will take up, confirm, and complete it. The behavior of potash seems to especially invite further attention.

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## ADDRESSES.

THE COST OF AVAILABLE NITROGEN.<sup>1</sup>

By DR. EDWARD B. VOORHEES.

The use of commercial fertilizers has been one of the most important factors in the development of the farming interests in this country. The present annual consumption is, as near as can be estimated, 5,000,000 tons which, at an average cost of \$29.00 per ton, makes a total expenditure of \$145,000,000. This great quantity of fertilizer is being used for increasing the crops of grain, hay, potatoes, fruits and market garden crops. The money is expended for nitrogen, phosphoric acid and potash, and notwithstanding the claims made for superior brands and special formulas, the returns are due to the actual amounts of nitrogen, phosphoric acid and potash that these crops are able to obtain from the total in the fertilizers used.

The value of the increased crops made from the use of any one or more of these constituents is, however, measured both by the amount that the crop obtained, and the character of the crop obtaining it. A pound of nitrogen, phosphoric acid or potash, when used in making a crop of celery, or of asparagus, or of fruit, would be worth more than if used in making a crop of wheat, rye, or hay; furthermore, the value of the user of the nitrogen or other constituents bought in a fertilizer, is measured both by the amount that the immediate crop is able to obtain, and the proportionate amount of the total that would eventually be gathered.

Of the sum annually paid for the three constituents, nitrogen, phosphoric acid and potash, about 40 per cent. is paid for nitrogen, which is the only one of the three essential elements that is likely to suffer any considerable loss in use, as the experiments conducted along this line show, on the average, not more than 70 per cent. of the quantities applied, even in the best forms, is recovered in the crops.

The case is different with phosphoric acid and potash; these are not subject to serious losses, under good methods of soil management. Practically, these constituents remain in the soil until they are taken out by plants.

From the standpoint of crop, it is evident that the utilization of nitrogen is a much more important matter than the use of phosphoric acid and potash, although the further fact that a pound of nitrogen, capable of being used in a commercial fertilizer, and without regard to form, costs from four to five times as much as a pound of "available" phosphoric acid or of potash, is an additional argument in favor of greater care in its purchase and use.

Nitrogen as nitrate is the only commercial form soluble in water, ready for immediate use by most plants; nitrogen as ammonia is also a form soluble in water, but it is less available than the nitrate. A pound of nitrate and a pound of ammonia, being definite chemical compounds, are quite as good from one source as another.

Organic forms of nitrogen have to decay first, changing to ammonia and then to nitrate, and are therefore less quickly available; besides, they vary in their rate of availability according to the source of supply and their physical character. Materials which are likely to decay quickly, as dried blood, dried meat, dried fish and cottonseed meal, do show a high rate of availability, while forms like ground leather and ground peat show a very low rate of availability. A pound of organic nitrogen varies in availability, therefore, according to its source, whether derived from dried blood or peat, or from intermediate products.

Since nitrogenous materials are variable in their rate of availability, that is, the rate at which the nitrogen in them may be absorbed by the plant, the farmer desires to know the dependence that can be placed on the different materials; he

<sup>1</sup> Delivered before the Division of Fertilizer Chemists, Boston meeting, American Chemical Society.

wants available nitrogen. Hence, the chemical and physical characteristics of the various forms of nitrogen have been made the subject of every considerable study and investigation, in order that at least approximate values in respect to availability may be attached to each form. Sufficient work has been done thus far to establish a pretty safe relationship between the nitrate, ammonia and organic nitrogen, in the form of dried blood. It has not been possible, yet, to investigate fully all of the various forms of organic nitrogen, so as to assign an exact value for the different materials.

The very extensive investigations conducted by Dr. Paul Wagner, at Darmstadt, Germany, show that for the crops tested by himself and others, namely, barley, oats, rye, wheat, mangels, sugar, beets and potatoes, there was returned in the harvest 62 parts of nitrate nitrogen for every hundred parts applied, 44 parts of ammonia nitrogen for every 100 parts applied, and 40 parts of organic nitrogen for every hundred parts applied as dried blood. In no case is the recovery equal to two-thirds of the nitrogen applied; besides, there are wide variations in the amount recovered in the different forms.

In 1898, plant nutrition experiments were begun at the New Jersey Station, one object of which was to study the "relative availability" of these three forms of nitrogen, using a rotation of corn, oats, wheat and timothy; crops which, because of their long periods of growth, would be likely to absorb relatively large proportions of organic nitrogen. The results of these experiments for two rotations (10 years) are reported in detail in Bulletin 221, and show that the recovery for nitrogen as nitrate was 62.09 parts per hundred, for the nitrogen as ammonia 43.26 parts per hundred, and for organic (dried blood nitrogen) 40 parts per hundred. These results agree almost exactly with those obtained by Dr. Wagner and his associates. With the returns from nitrate, the highest recovery regarded as 100, the relative availability of the nitrogen as ammonia would be 69.7 and of nitrogen as dried blood 64.4.

These figures possess a very great practical significance as they have a direct bearing upon the economical purchase and use of the nitrogen contained in the fertilizers now offered upon the market.

Commercial conditions fix the price of the various nitrogenous materials, and the cost to the farmer of any one form is not measured by its usefulness to him, but by the cost in the market; that is, there is no strict relationship between commercial and agricultural values.

It happens that at the present time, a pound of nitrogen in the form of nitrate or of ammonia costs the farmer less than a pound of organic nitrogen; that is, the nitrogen possessing the highest rate of availability as nitrate is less expensive to him than dried blood nitrogen, or even that derived from low-grade nitrogenous materials, which do not possess any definite rate, and which must, on the average, show a much lower rate of availability than dried blood, because the mixtures contain nitrogen derived from many sources, not uniform in their content of nitrogen or in their physical character or constitution.

Garbage tankage and tanned leather scraps, for example, are used in large quantities, some of the larger eastern fertilizer factories using several thousand tons per year. The nitrogen in these products is admittedly much less available than is that in dried blood, and its cost to the manufacturers is, according to present quotations, but little more than one half as high.

The Experiment Station has since its establishment consistently urged the farmers, in their purchase of fertilizers, to be guided not only by the quantities of the constituents present in the mixture offered, but also by the kind that is used in them, pointing out the importance of selecting brands which contain high percentages of available plant-food, more especially of nitrogen, because of its relatively greater importance, or its higher cost. The results obtained in the investigations reported

in Bulletin 221 emphasize very strongly the wisdom of such advice in reference to the expensive and elusive element, nitrogen.

A concrete example will make clearer the economic phases of the question. The analysis of the various brands sold in the State in 1909, and reported herewith, shows 2.57 per cent. of total nitrogen, divided as follows:

Nitrate.....	0.48 per cent., or 19 per cent. of the total.
Ammonia.....	0.77 " " 30 " "
Organic.....	1.32 " " 51 " "

Assuming that the forms of organic nitrogen used in these brands were as good as dried blood, it would require 1.55 pounds of the nitrogen to furnish as much "available" nitrogen as is contained in one pound of the nitrate nitrogen, and 1.43 lbs. of the ammonia nitrogen to furnish as much "available" nitrogen as is contained in one pound of the nitrate nitrogen. Yet, because of commercial conditions, the farmer paid a higher price per pound for his organic nitrogen than he paid for his nitrate and his ammonia nitrogen; using the same relations that exist in the commercial cost of nitrogen, the actual prices paid were, for organic nitrogen 26.52 cents per pound, ammonia nitrogen 23.73 cents and nitrate nitrogen 23 cents. At these prices, the nitrogen purchased in that year cost \$1,157,400. If, however, the returns from the different forms of nitrogen were in the same proportion, as indicated in the experiments, which must be admitted to be relatively correct for nitrate and ammonia, and assuming that the organic was as good as that in dried blood, the cost of the "available" nitrogen in the three forms actually was

For organic.....	41.12 cts. per lb.
For ammonia.....	34.04 " "
For nitrate.....	23.00 " "

while the farmer should have paid, on the basis of availability,

For organic.....	14.81 cts. per lb.
For ammonia.....	16.03 " "
For nitrate.....	23.00 " "

and a saving of \$383,940 would have been effected. If, therefore, instead of buying organic and ammonia nitrogen, nitrate only had been purchased, the same gain in crop from the use of the nitrogen could have been purchased for \$773,460 instead of \$1,157,400.

Assuming that practically the same relations existed for all the fertilizers made and sold in the whole country, this year, the actual cost of the nitrogen was over \$60,000,000 while on the basis of available it should have cost but \$43,000,000. It may be argued that the availability of the organic nitrogen is greater in the warmer climates of the South, where the bulk of the fertilizer is used; this may be true, but is probably counterbalanced by the fact that a much larger proportion of the nitrogen used there is in organic forms. It is a fact, too, that the present high cost of cottonseed meal has encouraged a larger use of the tankages and other lower grade nitrogenous products.

The point of importance, therefore, is the price that is paid for the organic forms. In the above discussion, it has been assumed that the organic nitrogen contained in the fertilizers has been derived from dried blood, or from other materials quite as good. As a matter of fact, however, dried blood does not constitute even a large proportion of the organic nitrogenous materials used, the bulk of the nitrogen being derived from products of a lower grade. Various kinds of meat and bone, tankage, dried fish, fish scrap, cottonseed meal, garbage tankage, leather meal and even peat are used to supplement products of the higher grade. These, while genuine nitrogen carriers, have been shown to have a wide range in availability, the leather and peat rating in availability as low as 4 in comparison with nitrate as 100.

It may be urged, first, that these products possess a value as sources of nitrogen; and second, they are valuable as absorbents and in improving the texture of mixtures containing



nitrate, acid phosphate and potash salts, as mixtures of chemicals only cannot be applied by machinery; and third, that proper conservation of natural resources demands that waste nitrogenous materials should be utilized. The points are *conceded*. The Experiment Station does not discourage, but strongly encourages the utilization of waste products containing nitrogen; it would be false to its duty to the farmers, however, if it did not clearly point out to them what is known of the relative agricultural value of such products. It is not solely a question of use, it is a question of cost. The cost to the farmer of a pound of nitrogen in these materials, of a value lower and more variable than the nitrate and ammonia, should be lower rather than higher than for nitrate or ammonia.

It is not economy to save refuse nitrogenous materials, if the cost of the nitrogen to the farmer is greater and his returns less than may be obtained by the use of nitrogen from materials of known value. Farmers have been and are now spending thousands of dollars for nitrogen for which they do not receive a proportionate return.

To the farmer, it is purely a business proposition. He buys nitrogen, in order that he may get a return in crop; if in one case 100 pounds of nitrogen contributes 60 pounds to the crops upon which it is applied and in another 100 pounds contributes but 40 pounds to the crops, the purchaser should not pay the same for the second as for the first, for if he did so he would pay 50 per cent. more per pound for his "available" nitrogen; that is, if the cost of the first hundred pounds were \$15, the second hundred should cost but \$10, when the basis of value is the amount available in each.

#### THE RELATION OF THE CHEMIST TO PROPRIETARY MEDICINES.<sup>1</sup>

W. A. PUCKNER, Secretary, Council on Pharmacy and Chemistry of the American Medical Association.

That the composition of proprietary medicines differs widely from that which is claimed for them by their manufacturers or owners has been given wide publicity through the enforcement of the Pure Food and Drugs Act and the exposures which which have been published in the *Journal of the American Medical Association's* Propaganda for reform in Proprietary Medicines. As a result of this publicity the public, and more particularly the medical profession, has become suspicious of statements made and is inclined to look for evidence which will substantiate the promoter's claims. This demand the manufacturers (promoters, owners) have attempted to meet in two ways: the large firms have employed a staff of chemists and have advertised that their products are duly examined and tested before being offered for sale. The degree of credence which is given to the firm's protestations of honesty and reliability has to no small extent depended on the professional standing of their chemists. While it is to be expected that the employees of a firm will incline to a high opinion of that firm's products, the reports of analysis or examination vouched for by such chemists of reputation as A. R. L. Dohme, J. M. Francis, A. B. Lyons, C. E. Vanderkleed, and other chemists closely identified with progress in pharmaceutical chemistry are generally accepted without question. This condition of affairs is satisfactory to all concerned but particularly so to chemists. As secretary of the Council on Pharmacy and Chemistry of the American Medical Association, I have had ample opportunity to see the increased reliance which is placed on the services of chemists. Formerly it was often quite evident that questions dealing with, the chemistry of medicinal products had been decided by the office force without consulting with those who were competent to decide the points involved. To illustrate the lack of coöperation between the scientific departments of

pharmaceutical manufacturing houses and the commercial end (evidently because the value of the scientific staff was not appreciated), it may be mentioned that a firm which had in its employ one of the chemists just referred to, offered to supply to the Council the structural formula of an iron protein compound of rather indefinite composition. To-day such questions are placed in the hands of those who are competent to decide them, the chemists. In this and in many other ways it is plain that the manufacturer relies to a very large extent on the chemist to demonstrate the reliability of his wares.

While the large manufacturing houses thus rely on the chemists in their employ, many smaller concerns, often aptly called "pseudo-chemical companies" do not regularly employ chemists. Although there is no sharp line of demarcation, these establishments may be divided into two classes: those who belong to one class, though often not overly conversant with the products which they sell, are entirely honest and sincere, and submit their products to commercial chemists or "professors of chemistry" for analysis in order to obtain certificates which will vouch for the quality of their goods.

Although there is a tendency to use a report of an analysis of a certain specimen of a product as an indication that all other lots of this product are of the same composition, and in this way to create a false impression, the employment of chemists to check the quality of medicinal products is to the best interest of all concerned. It helps the dealer to sell his goods, it ensures to the buyer their quality and it has helped to bring about a more general appreciation of the value of the science of chemistry.

While the manufacturers of, or dealers in, proprietary products just referred to, make use of the chemist in a perfectly legitimate way, this can not be said of all who are so engaged. A very large proportion of those engaged in the sale of proprietary medicines apparently believe that "all is fair in love and war" in the exploitation of medicines, and who have regard for the truth only so long as the telling of it will help the sale of their goods. When these concerns seek the services of a chemist it is less with a view of learning the truth regarding their products than to obtain good advertising copy. These concerns are willing to pay liberally for the right kind of a chemical analysis, that is, for a report which in its entirety or in part will look well in print. The way in which these concerns regard the chemist and his work is well brought out in an editorial which appeared in the *The Druggists' Circular* (October, 1908). Here it is related how a chemist was approached with the request to sign a report of an analysis and to pocket the fee without going through (what appeared to the one who wanted the analysis) the useless formality of making any examination of the product referred to in the report submitted to the chemist for signature. While few chemists will be tempted by such crude efforts at bribery, not all are proof to a more refined invitation to certify to that which is not the truth. By this I refer to the temptation to make out a report which emphasizes all the good points of a product, to minimize or to omit all that is derogatory to it and in other ways to make the report satisfactory to him who wants to use it in the exploitation of the remedy. When it is considered that the patronage of these concerns can be retained only by writing reports that will look well in print, it is not surprising that so many certificates of analysis give no material information in regard to the medicine which they are designed to advertise but can be used to create or perpetuate a wrong conception regarding the nature of the product.

If the report as a whole is not satisfactory, the exploiter of the proprietary medicine will of course not hesitate to use any part thereof which will make good advertising material even at the risk of utterly misrepresenting the actual findings of the chemist, as shown by the report.

<sup>1</sup> Delivered before the Division of Pharmaceutical Chemists, Boston Meeting American Chemical Society.

Since not only the reputation of the individual chemist, but also the reputation of chemists as a whole, will suffer through association with the exploiter of proprietary medicines as just described, I deem it of interest to offer the following illustrations of the way in which chemists are used as a means of exploiting a medicine in a way which discredits our profession.

In the *Journal of the American Medical Association* (October 13, 1906) the composition of a preparation known as Waterbury's Metabolized Cod-liver Oil compound was discussed. It was there stated that the product did not show any fat globules under the microscope and that it was therefore not an emulsion, that it was acid in reaction and did not become turbid on the addition of strong acids and hence was not soap or a saponification of fat, that it did not become turbid on dilution with water and hence could not contain more than traces of a fatty acid. In view of this evidence and because of confirmation by chemical examination it was stated that the preparation, although claimed to contain the product "obtained by the action of fat-splitting ferments on cod-liver oil," represented no (or at most a mere trace of) cod-liver oil. In an attempt to offset this damaging evidence the Waterbury Chemical Company published in the form of advertisements, a number of chemists "reports of analysis" which, more or less directly, denied the truth of the damaging report of the *Journal of the American Medical Association*. One advertisement purporting to be a report signed by a professor of chemistry in a college of pharmacy is rather indefinite and vague, but it contains the phrase "of course we know that the finished product contains metabolin" which, while meaningless, no doubt impressed many as some sort of a confirmation of the truthfulness of the claimed presence of "metabolized cod-liver oil." Another advertisement bearing the fac-simile signature of a professor in a western university certified that the product contained the following imposing list of constituents without giving any quantities:

Maltose and Reducible Sugars; Oils and Fatty Acids; Glycerine-Alcohol-Acetone; Acids including Hypophosphoric, Phosphoric, Tartaric, Acetic, Sulphuric and Hydrochloric; Proteids (soluble and of variable composition); Benzaldehyde very small quantity present; Bitter Principle, not Alkaloidal, vegetable character; Ferments—Enzymes, etc., including various Organized and Unorganized Ferments; Inorganic Salts, Iron, Sodium, Calcium; Further the report states that "In the fats extracted there is present free fatty acids, in which Palmitic, Stearic and Oleic Acids are identified."

While chemists will have no difficulty in assigning its real value to any report of an analysis which does not give quantities, physicians no doubt were duly impressed by the statement regarding the presence of a large number of constituents including "oils and fatty acids."

In a third advertisement the statement made in the *Journal of the American Medical Association* that the product when acidulated remained clear was definitely challenged. The advertisement appears to be a reproduction of an analytical report and shows the signer to be a doctor of medicine as well as a doctor of philosophy.

Recently (October 9, 1909) the chemical laboratory of the American Medical Association published a report of an analysis which confirmed the statements made in the *Journal of the American Medical Association* (October 13, 1906). The report shows that a specimen of the preparation purchased in the open market contained probably not more than 0.1 per cent. and certainly not more than 0.3 per cent. of fatty acids and that, for all practical purposes, it should be considered devoid of cod-liver oil. Since then the federal authorities have brought suit to confiscate a shipment of the Waterbury product, the charge being in the main that it contains no cod-liver oil and is therefore misbranded.

It is thus seen that the certificates of chemists have been used

to aid in the sale of a fraudulent product. That this is contrary to the best interests of the public, our profession and of the signers of the reports goes without saying. It also is quite evident that the manufacturer of the product deliberately made use of the reports to misrepresent the facts. But it seems to me that the signers of the reports are not without blame since the misuse of chemists' certificates tend to discredit the entire profession; and since the abuse is quite common I consider it my duty to call attention to the matter by pointing out how far the signers of the reports were at fault or at least were injudicious.

Granting that the particular specimen of the product which the signer of the first report examined did contain any appreciable amount of the products produced by the action of digestive ferments on cod-liver oil, the application of the term "metabolin" to such a mixture seems inexcusable. Whether the term was used to impress the manufacturer with the scientific attainments of the writer of the report or with a view of furnishing suitable advertising material to the manufacturer, the chemist must have known that its use was unwarranted. From a letter received in reply to my request for information as to the method used to determine the amount of "metabolin" and the amount actually found (information which it is needless to say was not forthcoming), I am inclined to believe that the chemist was much surprised and chagrined to find that a portion of a letter written to the manufacturer was used as advertising copy.

According to the chemist, whose signature appeared in connection with the second advertisement mentioned, publication of his report was authorized only on condition that the complete quantitative analysis be furnished to physicians who asked for it. This being the case and granting that all of the constituents mentioned in the imposing list (including oleic acid, the demonstration of which has baffled chemists for fifty years or more) were actually identified in the specimen examined, also granting that it was not made out with a view of impressing the manufacturer with his ability, no specific fault can be found with the chemist's report but the chemist should have known that it would be used to mislead others in regard to the composition of the preparation.

While at first it would appear as if the statements of the chemist's report in the third advertisement were refuted by the published analysis of the chemical laboratory of the American Medical Association, and by the action of the federal authorities, this is not the case. Instead it is probably but another illustration of the often noted variability of proprietary medicines. The specimen reported on by the laboratory of the American Medical Association, and which was found to be practically free from fatty acids, was purchased on the open market. On the other hand, the specimen reported on in the third advertisement, according to the statement of the chemist to me, contained about three per cent. of fatty acids. From this it is evident that the chemist did nothing more than report his findings. But in view of his training as a chemist and as a physician he must have recognized that the preparation did not contain enough cod-liver oil to give it any value as a cod-liver oil preparation. Further, he must have known that his report would be used to mislead physicians in regard to the actual composition of the preparation.

To show the tendency of analysts to write reports which will make good advertising copy and to show how such enthusiastic reports may later place the chemist in an embarrassing position, the following is given: The Council on Pharmacy and Chemistry of the American Medical Association some time ago (October 20, 1906) published a report which stated that a certain product, Tyree's Antiseptic Powder, did not possess the composition which its manufacturers had claimed it to have. As in the case of the Waterbury product so in this instance the manufacturer

attempted to offset this by publication of a report of a chemist. In this analytical report which deals with the composition of the product and the purity of the materials used in its preparation it is stated that the product contains, among other things, zinc sulphate and phenol; that these two substances "of course react to form zinc phenol-sulphonate." While it is a rather common misconception that phenol and sulphates when dissolved in water react to form phenol-sulphonates, the statement in regard to its formation was so foreign to the subject of the analytical report that I wondered whether the analyst had really made this statement. Correspondence with the analyst brought out the fact that the statement was contained in the report made to the manufacturer. The analyst also informed me that he had advised the manufacturer that this statement was incorrect and should be omitted from his report. It should be added that the manufacturer, now (or at least quite recently) three years later, is still circulating the statement.

What has been said illustrates a general tendency to frame reports of chemical analyses in such a way as to create a favorable but incorrect opinion in regard to the product reported on. While the writers of such reports can rarely be accused of making any incorrect statements they often disguise or ignore the facts in such a way that their effect is the same as if a direct misrepresentation had been made. There is grave danger that the term "commercial chemist" may come to be generally interpreted as meaning a chemist who puts a commercial value on his reports; that is, a chemist whose favorable reports may be purchased. While many analysts are above reproach in this respect, the tendency is so general that individual chemists should be blamed for this condition. It seems to me that the time is ripe when chemists individually and through their societies should express their disapproval of a practice which is a discredit to the entire profession.

## NOTES AND CORRESPONDENCE.

### THE LENGTH OF A TECHNICAL PAPER.

The appeal of Mr. Albert E. Leach, on the editorial page of *THIS JOURNAL*, January, 1910, for greater brevity in the method of presentation of technical papers must be seconded unanimously by those who attend scientific meetings and, for the most part, likewise by readers of scientific journals. However, the abbreviations of strictly technical papers intended for publication, it must be conceded, if too much emphasized is quite apt to be overdone.

The articles appearing in *THIS JOURNAL* and in the *Journal of the American Chemical Society* are supposedly exact accounts of observations of chemical operations, with results, descriptions of chemical processes and presentations of chemical theory. The science of chemistry has been expanded to such enormous proportions that it has long since become impossible for any one mind to have more than an elementary knowledge of all the different branches. It is therefore manifestly impossible for any one, however broad one's interests and however great one's desire for information, to read with any great degree of understanding all of the more technical articles appearing even in these journals. For the author to so popularize his articles that such a reader can not only understand but can enjoy the perusal thereof would necessitate his pruning out the more technical and, therefore, the most important, portions of his contributions.

The very excellent method of printing adopted by the *Journal of the American Chemical Society*, involving the use of different sized type, emphasizes the more important matter and makes easy the perusal of technical papers by the casual reader.

Let technical papers be written by the specialist for the specialist. "Padding," which is easily recognizable, should

be condemned, but let scientific observations be recorded with special attention to detail so that, should occasion arise, work described can be repeated and processes portrayed can be reproduced with accuracy.

To record results is not sufficient, though to the non-specialist they are of prime interest. The specialist wants to know how the results were got and he demands that the details be presented with such a degree of elaboration that he himself can duplicate the results. Otherwise, he can arrive at like results only after experimentation and investigation to discover the methods.

Who is interested in an analytical method except the man who expects to use that method? Or who becomes enthusiastic over the derivation of some complex chemico-mathematical formula except the man who is himself employing such a formula, either as an end in itself, or as a means to an end?

Let him who craves popularized science read those journals devoted thereto, and let him who wants the bare results of chemical research read the *Abstract Journal of the American Chemical Society*. But let us have journals devoted to the sort of publications which will enable the specialist and the investigator to find expert knowledge first hand and in detail.

J. W. TURRENTINE.

### THE DETERMINATION OF PHOSPHORIC ACID BY THE OFFICIAL VOLUMETRIC METHOD.

The Official Volumetric Method for the determination of phosphoric acid is very popular among chemists who have a large amount of work to do on account of its rapidity and ease of manipulation. Some, however, admit that they cannot use it with any satisfaction, and cling to the old "magnesia process." Others use it for low percentages and rough factory tests, and check frequently with the gravimetric method.

The writer has had about fifteen years' experience with the method, and has observed the work of many different chemists during the time; the result of this experience shows conclusively that the method is not entirely reliable under all conditions. In the first place, the process as outlined in the revised Bulletin of "Official Methods of Analysis" is faulty. Here the chemist has not only the option of making the solution by several different methods, but he is at liberty to precipitate with the molybdic solution either at 65° or 45° or even in the cold, and any one who has had experience knows that if other conditions are the same, these different temperatures will have a marked influence on the percentages of phosphoric acid obtained. There is considerable doubt whether the precipitate formed is always of the same composition even when great care is taken to have all the conditions just right; at any rate, it only takes some slight deviation from the accepted practice to materially affect the results. The presence of sulphuric acid tends to make the results high, and it is evident that if sulphuric acid is used as a solvent, or even the varying quantities which are present in fertilizers will have some slight influence on the accuracy of the determinations. High temperatures give high results, and low temperatures low results; the presence of ammonium nitrate in varying quantities also has an appreciable influence. Other conditions might be mentioned, but these are sufficient to illustrate the point; that is, the method is too delicate for the average analyst who turns out a large number of determinations. There is no use in attempting to follow the printed directions and expect accurate results. The only way to obtain good work is for each analyst to take some standard samples of known composition and adjust the working conditions in such a manner that correct results may be obtained. It will be necessary for every chemist to determine these conditions for himself, and carefully adhere to the same routine in his future work. If this plan is followed, a good analyst should be able to do fairly accurate work, but even then there will



occasionally be results which cannot be accounted for. In my laboratory, there is never a set of phosphoric acid determinations made by this process without carrying along a check sample; this serves as a safeguard to indicate any erratic condition which may have crept in. In addition to this, frequent gravimetric checks are made. No important analyses involving the settlement of large contracts are ever entrusted to the volumetric process.

It is not intended to imply that it is impossible to get accurate results by this method, but to point out some of its weak points, and to show how ill adapted it is for strictly accurate work under the usual working conditions of commercial or state inspection laboratories. While, therefore, the method is useful for certain classes of work, it is unfortunate that it was adopted as an "Official Method," by the A. O. A. C. to be used at the option of the chemist as the basis of settlement in the analysis of large and important purchases of material, or for the testing of fertilizers by our Agricultural Departments where slight deviations from the guarantee involve severe penalties, or otherwise affect the business of the manufacturer by publishing the results in bulletins which are distributed broadcast to the consumers.

F. B. CARPENTER.

#### UNIFORM ANALYTICAL METHODS FOR PHOSPHATE ROCK.<sup>1</sup>

As the discrepancies between the results of chemists in the analysis of phosphate rock have often been the cause of disputes between buyer and seller, sometimes resulting in costly litigation and usually ending in a feeling of diminished confidence by the manufacturer for his chemist, the National Fertilizer Association, at their annual meeting at Atlantic City in 1908, appointed a committee to examine the various analytical methods for phosphate rock then in use, with a view to the adoption of methods which would yield uniform results.

That year four sets of phosphate rock samples were prepared, consisting of Tennessee brown, Tennessee blue, Florida and South Carolina rocks. These were distributed among the chemists of the National Fertilizer Association and the commercial chemists who make a specialty of fertilizer analyses. Each chemist was instructed to determine moisture, phosphoric acid and iron and aluminum oxides, using the routine methods of his laboratory, and to return a complete report of his results, together with a copy of his methods. Samples were sent to approximately fifty, and reports were received from thirty-one.

The results of this work were published in detail in pamphlet form by the Association.<sup>2</sup> A study of the tables of results confirmed the existence of serious differences in the results of various laboratories, which could not be laid to differences in samples. The samples had been prepared with extreme care, and were as nearly uniform as it was possible to make them.

In the report of the Committee to the National Fertilizer Association, made in October that year, it was tentatively recommended that for referee work the Official gravimetric method be used for phosphoric acid and that in the methods for iron and alumina then in use, the solvent be hydrochloric acid (1-1) until the question of the effect of pyritic iron in acidulating could be definitely solved.

In April, 1909, another sample of phosphate rock was distributed together with a set of methods, which were based on a study of the results of the previous year and on comments and suggestions of the cooperating chemists. The sample was a mixture of Tennessee brown and blue rocks, and of

Florida pebble. This sample was prepared with every possible precaution to ensure uniformity, and as in the previous samples, was to be used without further grinding or handling, having been ground to the requisite fineness during the preparation of the sample.

Samples and instructions were sent to approximately fifty chemists, but reports were so slow in coming in that at the time of the meeting of the National Fertilizer Association at Atlantic City, July 6th and 7th, the committee was able to make only a preliminary report on the work done this year. This report was published in the August number of *This Journal*, in 1909. A few additional results have been received since, but they caused no improvement in the general character of this work. In all, reports were received from thirty-one chemists.

It is to be regretted that the results obtained this year do not show a more decided improvement over those of last year than is the case. The committee does not believe that the point has been reached where methods to be used as official in referee work can be definitely recommended.

An interesting point shown in the results received, is that those analysts who are chiefly and solely engaged in referee work agree very closely and that the greatest variations occur in the results of some of the chemists employed in the laboratories of the various manufacturers or retained by them. It is difficult to conceive how such differences can exist as shown, for instance, in the determination of moisture, considering that it is apparently one of the simplest determinations a chemist has to make. Yet some of the worst discrepancies are to be found in the results reported on this determination.

The committee could undoubtedly have chosen chemists for this work whose results would have been quite uniform, but the idea of this work is to arrive at methods which shall be so clear and so definite that any analyst should obtain results agreeing very closely with those obtained by any other analyst using the same methods.

A final report to the National Fertilizer Association has not been made as yet. Regarding the methods to be considered, there seems to be no reason for changing the proposed method for moisture as outlined in the instructions sent out this year. Regarding the phosphoric acid, nothing has developed to change the tentative recommendation of the Committee in favor of the Official gravimetric method including a proper method of solution of phosphate rock. While the results by the volumetric method show a marked improvement over those of last year, it does not seem advisable to recommend it in preference to the gravimetric method or even as an alternative method for referee work. The Wagner citrate method and others proposed do not seem to offer any advantages over the Official gravimetric method. Regarding the determination of iron and aluminum oxides, the committee tentatively leans toward the caustic potash method. The great irregularity of the results received by the acetate method seems to offset the good agreement by those accustomed to using it. Objection has been made to the apparently complicated character of the caustic potash method, but this is not founded on fact. The determination of iron by the permanganate method is certainly not a difficult nor complicated one, and the number of solutions required need not confuse any competent analyst. The most serious objection to the caustic potash method seems to be that a correction is required for the alumina, silica, etc., but the objection to blank determinations holds good in many other methods, as for instance in the determination of nitrogen.

The committee believes that this work should be taken over by the Division of Fertilizer Chemists of the American Chemical Society and wishes to urge upon the members of the Division

<sup>1</sup> Read before the Division of Fertilizer Chemists, Boston meeting, American Chemical Society.

<sup>2</sup> *This Journal*, 1, 41.

the great need of immediate and effective coöperative work on this subject. A large stock of the samples which were distributed this year is still on hand and should prove of the greatest value to the coöperators in this most important work. As stated in the preliminary report on the work of this year, the committee believes that standard methods alone are not sufficient to ensure uniformity. It is evident that considerable familiarity and experience with any method is required before dependable results can be obtained by it. For this reason it seems that standard methods should be accompanied by standard samples so that every chemist interested can obtain them for the purpose of verifying his work from time to time.

C. F. HAGEDORN.

## BOOK REVIEWS AND NOTICES.

**Beet Sugar Making and Its Chemical Control.** By Y. NIKAIIDO, B.Sc., M.A. Easton, Pa.: The Chemical Publishing Co., 1909. Octavo, xii + 354 pp., 65 illustrations. \$3.00 net.

The author states that this book is intended as an aid to those engaging in beet sugar manufacture, who lack systematic technical training in the matter.

This the author undertakes to supply in an unusual manner in a series of chapters on general chemistry and sugar house processes, both manufacturing and analytical, which view the entire field broadly and specifically. After a chapter on definitions of chemical terms follows one on the non-metallic elements. The novel method of presentation is instanced here, where under "Nitrogen" we find a discussion of ammonia in beet juice and the difficulties arising therefrom; under "Chlorine" directions for preparation of normal hydrochloric acid and other normal solutions, acidimetry, alkalimetry, etc.

Chapter III, in similar manner, deals with the principal metallic elements, giving various collateral information about lime and iron and an analytical method for the determination of copper. Then follow chapters on Organic Chemistry (30 pages) and Cane Sugar (17 pages) setting forth the classification of organic compounds and giving the properties of sugar and its compounds met with in beet sugar manufacture.

The well-arranged chapter on the "Polariscope and Its Accessories" is accompanied by numerous well-designed illustrations, and treats the subject in a clear, comprehensive manner. Other laboratory apparatus is discussed and directions given for determination of sucrose, total solids and purity.

Chapter VIII deals with the "Practical Operations of the Beet Sugar House" and describes in considerable detail the operations, from the harvesting of the beet to the last process in making white sugar and the recovery of sugar from molasses. This chapter, giving the limits within which good work should be conducted at the various stations, will be found of considerable value to those engaged in this work. A final chapter on "Special Analysis" (39 pages) takes up all the analytical determinations ordinarily needed, not already described, with formulae for calculation of results and many examples to make the matter plain.

An Appendix contains a few tables most commonly used in sugar work.

In viewing the book broadly it is a clever compilation of material from a dozen or more authoritative treatises on various subjects so brought together as to bear most closely on beet-sugar making, considered chemically.

The book is essentially a mixture that one could wish to see

sorted out more thoroughly so that all the analytical matter would appear together and so be more directly accessible. It is a question whether the theoretical part is not largely over the heads of those who have had no previous technical training, but it is all very suggestive and will doubtless prove a grateful reminder to those already conversant with the subject.

W. D. HORNE.

## INDUSTRIAL AND TRADE NOTES.

*Air-Nitrates in Germany.*—Consul-General A. M. Thackara, of Berlin, answers as follows the queries of an American correspondent regarding the manufacture of air-nitrates and the status of farming in Germany:

Atmospheric nitrogen is utilized in making nitrates for fertilizing purposes, in accordance with two general systems in Germany, as well as in Norway, Italy, and other European countries, and in Canada. (1) The formation of the so-called calcareous nitrogen (kalckstickstoff), which has the chemical formula  $\text{Ca}(\text{CN})_2$ , and which is formed by passing nitrogen over heated calcium carbide or through a heated mixture of lime and charcoal, and (2) the direct combination of the elements in the air—oxygen and nitrogen—by the use of the electric spark and the formation of nitrate by bringing these combinations into contact with the proper calcium or other compounds.

There are several processes by means of which the nitrogen, which combines with the calcium carbide in the formation of calcareous nitrogen, is separated from the oxygen of the air. One is by passing air over the copper coils by means of which the oxygen is removed. Another process is to obtain free nitrogen by the partial evaporation of liquefied air. The great expense attending this latter process renders it impracticable, and the nitrogen so obtained is still much mixed with oxygen compounds. Nitrogen is also obtained by one German firm in Hamburg and Hanover by cooling the gases of combustion and removing the impurities by passing the gases through retorts filled with copper and copper oxides and then through some substance that absorbs the carbon dioxide.

The so-called calcareous nitrogen obtained by the various processes is a grayish substance containing about 20 per cent. nitrogen. As a fertilizer it is generally supposed to be as efficient as ammonium sulphate and but little inferior to saltpeter. The exact effect of the cyanide in the compound is as yet not understood. By heating, the whole of the nitrogen in the compound is changed into ammonia, from which ammonium sulphate may be formed. The practicability of the production of calcareous nitrogen depends upon cheap power supply, and hence the plants are generally located where water power is available. The substance is produced in many different countries and the estimated total production for 1908 was about 45,000 tons.

The second system by which nitrates are obtained by the direct combination of the oxygen and nitrogen of the air is much more recent in its development than the above. After numerous attempts had been made in various countries, the Norwegian inventors, Birkeland and Eyde, finally succeeded in making the process industrially practicable (described in a monograph on "Manufacture of Air-Nitrates" recently published by the Bureau of Manufactures). According to their system, the end of each of the electric poles through which a current is passing is exposed to the action of the magnet which causes the electric spark to spread out into a disk-like flame. This flame is surrounded by some material that resists combustion,

thus leaving a disk-shaped enclosure through which the atmosphere is sucked. As the temperature at which this reaction takes place is very high and as the atmosphere passes comparatively rapidly through the flame, only from 1 to 2 per cent. of the elements in the air is transformed. The compounds formed begin to decompose when their temperature is lowered, and therefore methods are devised to rapidly decrease their temperature to the point at which they can form more stable products. For this purpose the compounds are passed through an evaporation apparatus, and after their temperature has been reduced to about 50 degrees Réaumur they are passed into an oxidation chamber and oxidized into nitrogen dioxide, from which the nitrates are made. The farthest advance in this system has been made in Norway, principally by the firm of Birkeland & Eyde, and in factories located at Notodden, Svålgef, and Christiansand. A similar system in Germany is used at the "Badische Anilin- und Soda-Fabrik" at Ludwigshafen am Rhein. The nitrates so formed are quite pure and have thus far been consumed principally in the industries, only a small quantity having been used as fertilizers.

#### COST OF PRODUCTION WORKS OF REFERENCE.

The cost and the volume of production of each system depend upon the availability of cheap power, and the production of calcareous nitrogen also depends upon the prices at which lime and coal or charcoal are available. One estimate places the cost of the production of calcareous nitrogen containing 20 per cent. nitrogen at 270 to 315 francs (\$52.11 to \$60.79) per metric ton (2,204.6 pounds). This would make the nitrogen in the compound cost 26 to 30 cents a kilo (2.2 pounds), while the cost of the nitrogen in compounds formed by the direct combination of the elements in the air is generally conceded to be less. The experiments made with fertilizers of either system, in comparison with Chilean salt-peter, are generally favorable to the artificial product. In sandy soil the calcium nitrate formed by the direct combination of the elements in the air brought even better results than the Chilean salt-peter.

A description and illustrations of the mechanical devices in use in the electrical system of producing atmospheric nitrogen is published by one Witt in *Das neue Technisch-Chemische Institut* for 1906, which may be procured for 2 marks (\$0.476) at the Weidmannsche Buchhandlung, Zimmer-Str. 94, Berlin, and a cursory description of the various processes in use in both systems, as well as the numbers of the various patents covering the same, is given in *Stahl und Eisen* for May 19, 1909, published in Dusseldorf. Copies of the German patents may be procured at 1 to 2 marks each (\$0.238 to \$0.476) through an American or a German patent attorney.

Another book giving an exhaustive description of the technical and industrial application of atmospheric nitrogen is issued by Doctors Donath and Frenzel, of the Technical High School at Brunn, and can be obtained from the book-dealer A. Seydel, Königgrätzer-Str. 31, Berlin. The price of this book is 7 marks (\$1.67).

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*Nitrates in Norway.*—Supplementing previous articles in *Consular and Trade Reports* on the manufacture of air nitrates for fertilizer in Norway, Germany, and Niagara Falls, Canada, it is learned from British consular reports that the industry is undergoing rapid expansion in the first-named country, where nearly \$15,000,000 will be invested. Though there are vast water powers in the United States running to waste, which could be utilized to produce this article, nothing has yet been done in that line, although this country is buying annually about \$15,000,000 worth of Chilean nitrates. The British consul's report from Christiania reads:

"Up till now about \$6,000,000 has been expended on the works at Notodden and Svålgef and the power stations under construction at Rjukan and Vamma. When all the works

are completed, at the end of 1910, \$14,600,000 will have been spent. A great point in connection with the development of this industry is that the opportunity has now arisen of opening up several industries in connection with the manufacture of nitrates, such as nitric acid, nitrate of ammonia, nitrate of potash, also sodium nitrate, which last is already being manufactured.

The Nobel syndicate, in conjunction with the Birkeland and Eyde Company, is now concentrating the weak acids, with the assistance of the gas furnaces, to an acid of such percentage as to become an article of transport, and further opportunities have thus been opened for export trade, especially from works with water power that are situated near the seaboard.

It is of interest to note that no coal is used in the production of salt-peter or other products here referred to. It is stated authoritatively that there is no probability for many years to come that the sale of salt-peter produced by the method practiced at the Notodden and Rjukanfoss works will be disturbed by competition with Chile salt-peter on the question of price.

#### LARGE ANNUAL PRODUCTION.

When the Rjukan Falls works are fully completed, they and the Notodden works combined will represent 240,000 horsepower, with a production of salt-peter representing an export value of \$6,164,000.

As time not very far distant time it is not improbable that the waterways and loughs between Skien and Notodden may be increased to such size as to allow sea-going vessels to load up at Notodden. Plans have already been worked out and are under consideration in connection therewith. At present everything has to be lightened to and from Skien.

The value of the output of nitrates in Norway in 1908 was about \$536,000, and the total expenses amounted to \$402,000.

The following are the companies that are producing, or will shortly produce, salt-peter from the air:

(1) The Norsk Hydro Elektrisk Kvaelfstof Aktieselskab, Christiania, who are the owners of the Notodden Salt-peter-fabrikker, the power of which (35,000 h. p.) is supplied from the Svålgef. The capita' of the company, which is French, is \$7,890,000.

(2) The Vammafos (Vamma Falls) Company, whose salt-peter works are now under construction. This company is a separate company, but half of its shares are said to be owned by the Norsk Hydro Elektrisk Kvaelfstof Aktieselskab; some of the preference shares are in the hands of Norwegians. The amount of the capital can not be stated.

(3) The Rjukanfos (Rjukan Falls) Company, whose salt-peter works are also in course of erection. The capital of the company, which is one half French and the other half Scandinavian and German, is \$3,376,800. This capital has been furnished by some of the shareholders of the Norsk Hydro Elektrisk Kvaelfstof Aktieselskab and of the Kraft Aktieselskab, but the company is an independent one.

(4) The Matre and Tyin waterfalls are owned by the Norsk Hydro Elektrisk Kvaelfstof Aktieselskab and by the Kraft Aktieselskab, but the companies formed in connection with these falls are two separate companies with separate administrations. Electro-technical works will probably be erected at both of these falls.

(5) Christiansands Elektrokemiske Aktieselskab, which is the property of the Badische Anilin- und Soda-Fabrik, Ludwigshafen, and has a capital of \$53,600.

*Chilean Nitrate Situation.*—Consul Alfred A. Winslow, writing from Valparaiso, under date of November 30th, reviews the conditions of the nitrate mining industry in Chile:

The nitrate industry in Chile is still in very bad shape, with no prospects of any immediate relief. The price of nitrate is very low, being only \$1.60 United States gold per quintal,



against \$2.13 in 1907, when the industry was flourishing. The different interests are cutting prices until many of the works have shut down because they can not produce nitrate at the present prices. There has been no concerted action since the combine was dissolved last April, and the outlook is not bright for this most important industry for Chile. This question is receiving much attention on the part of the National Government, and the President of Chile has just published a decree constituting a commission composed of the director of the division of nitrate in the Treasury Department, the president of the Sociedad Nacional de Minería, the professor of nitrate subjects in the National University, the Santiago delegate of the Nitrate Propaganda Association, the Assistant Secretary of the Treasury, and five members with a secretary, to be named by the President of Chile, which is to make a thorough study of the perplexing problems involved in the present unsatisfactory conditions of the nitrate business.

This commission is instructed to report to the Secretary of the Treasury on what means can best be employed to reduce the cost of production, on an organization for the sale of nitrate, on a systematic propaganda in the interest of an increased consumption of nitrate, and on a definite plan for the systematic location of claims in the nitrate fields, together with other matters that may present themselves.

For the first 10 months of 1909 there was an increased exportation of 2,415,396 quintals of nitrate over the same period of 1908, but at a great loss in receipts, which has cut down the profits to very small margins in all cases where they have not been entirely wiped out.

#### CONSUMPTION AND PRODUCTION.

A review of the Chilean nitrate trade by a British firm contains the following statistics:

The world's consumption for the past twelve months at 1,929,000 tons, against 1,732,000 tons in 1908, is highly satisfactory, showing, as it does, an increase of 11½ per cent., or 196,000 tons. Of this quantity the European Continent accounts for 1,354,000 tons against 1,275,000, an increase of 6 per cent. An increase of 7¼ per cent. is also shown by the United Kingdom, the figures being 111,000 tons, against 103,000. Consumption in the United States has not only recovered lost ground, but has beaten the previous best record of 355,000 tons in 1906 by 12 per cent. The figures are 398,000 tons, against 309,000, an increase of 29 per cent. Other countries account for 66,000 tons, against 45,000 tons, or an increase of 47 per cent. Production for the eleven months ended 30th November, at 41,106,660 quintals, against 39,236,640, shows an increase of 1,870,000 quintals, or 84,700 tons. Shipments for the twelve months to all parts amount to 2,085,000 tons, against 2,017,000, an increase of 68,000 tons.

*Trade in Antimony.*—As the new tariff law of the United States raised the duties on antimony in order to encourage its home production, interest attaches to the following report from Consular Agent Ernest L. Phillips, of St. Helens, on its manufacture in England mainly from foreign ores:

Basil Valentine said: "The shortness of life makes it impossible for one man thoroughly to learn antimony, in which every day something new is discovered." The crude ore stibnite or gray antimony was formerly mined at several places in Great Britain, but latterly this country receives most of its supplies from China, Australia, Chile, and Nova Scotia.

The process of extracting the antimony from the ore is a simple matter, but there are several processes employed. The crude and commercial antimony, the bulk of which used throughout the world comes from China and Japan, is the ore separated from associated earthy gangue, and this operation is performed by a simple fusion. From this there are two or three ways of obtaining the regulus of antimony. The raw antimony,

whether obtained direct from the ore or from the purified sulphide, must be calcined, in order to separate such impurities as arsenic, sulphur, etc. In the process of getting it direct, the ore is smelted together with some alkaline slag and old scrap iron. When this combination has completely fused, it is poured into conically shaped molds, and this mixture, after cooling, consists of impure antimony and sulphide of iron.

There are several methods used for purifying the regulus. One of the simplest is to charge each of the number of crucibles with this regulus along with soda, common salt, and pure oxidized antimony ore. When sufficient heat has been applied, the foreign impurities or metals become oxidized and scorified, and the star metal is thus obtained. Antimony is a bright silver gray metal; it is brittle and can be easily pulverized; it is valuable for the alloys it yields with other metals; the britannia metals, type metal, stereotype plates, Babbitt's anti-friction metal, and shot, all contain a certain proportion of this valuable commodity.

The exports of star antimony metal from St. Helens to the United States during 1908 amounted to \$40,419.

The importation of antimony metal into the United States during fiscal years ended June 30th has been as follows:

Country.	1904. Pounds.	1905. Pounds.	1906. Pounds.
Austria-Hungary.....	111,224	133,243	794,663
France.....	111,224	220,736	521,719
United Kingdom.....	2,124,660	3,070,522	4,521,797
Other countries.....	1,694,995	1,098,780	1,253,539
Total.....	3,930,879	4,523,281	7,091,318
Total value.....	205,908	312,332	795,398

Country.	1907. Pounds.	1908. Pounds.	1909. Pounds.
Austria-Hungary.....	1,156,027	459,564	67,427
France.....	422,322	1,116,225	1,108,189
United Kingdom.....	5,263,717	5,615,168	6,651,934
Other countries.....	1,968,131	855,159	1,703,217
Total.....	8,810,197	8,046,116	9,530,767
Total value.....	1,945,362	672,934	644,734

The unit value of the imports in each year per pound was as follows: 1904, 5.2 cents; 1905, 6.9 cents; 1906, 11.2 cents; 1907, 21.7 cents; 1908, 8.4 cents; 1909, 6.8 cents.

The imports of antimony ore averaged about 2,000,000 pounds for the fiscal years 1904, 1905 and 1906, while for 1907 it amounted to 3,053,082 pounds, but dropped to 1,684,774 pounds in 1908. However, in 1909 the imports increased to 6,021,877 pounds. The average value of the ore fluctuated heavily, in keeping with the price of the regulus or metal. The unit value of the ore imports in 1908 was 5.4 cents per pound. About one-half the ore in 1908 was secured from China, and about one-third *via* England.

Until the new Payne tariff act antimony ore was admitted into the United States free of duty, while three-fourths of 1 cent a pound was charged on the regulus or metal. The new customs law taxes the ore at 1 cent per pound, and the metal at 1½ cents per pound.

The Geological Survey states that the production of antimony in the United States during the years 1904 to 1908 has been as follows:

Year.	Short tons.	Value.
1904.....	3,057	505,524
1905.....	3,240	705,787
1906.....	1,766	602,949
1907.....	351	77,300
1908.....	Nil.	Nil.

A limited mining of antimony ore has been carried on in Nevada, though with the high prices in 1906-7, when the best grade of the metal reached 28 cents a pound, operations were

begun in Washington, Idaho, Utah, California, and Oregon. Many gold and silver ores are antimony-bearing, and in smelting the antimony combines with the lead of the charge, the product going on the market as antimonial lead. The alloy is used in type metal, babbitt, coffin trimmings, linings for acid tanks, toys, clock cases, and other articles for which a fairly hard metal to be gilded or otherwise finished is desired. Other uses of antimony are described by the Geological Survey:

Antimony is also used as an adulterant in solder and is considered a very objectionable element, especially when the solder is to be used for sealing cans holding provisions. Some antimony compounds are very poisonous, especially the organic compounds. The use of antimony salts and oxides is comparatively large, as shown by the importations (\$85,389 pounds worth \$105,234) in 1908. Antimony trioxide is used as a pigment in place of white lead, zinc oxide, etc., and seems to be gaining ground, especially in Europe. The trioxide is also used for making the glass used to coat iron in enameled ware, as a reducing agent in chemical work, and as a detector of alkaloids and phenols. Antimony arsenate, arsenite, trichloride, iodide, trioxide, trisulphide, pentasulphide, tartrate and antimony and potassium tartrate are used in medicine. The trichloride, also called antimony butter, is used in bronzing iron, especially gun barrels, as a mordant for patent leather, in coloring zinc black, as a mordant for silver, and in the manufacture of lakes particularly from dyewoods.

The double salts, antimony fluoride and ammonium sulphide, antimony and potassium oxalate, and antimony and potassium tartrate (tartar emetic) are used in dyeing.

The trisulphide is used in pyrotechnics for making "Bengal fire," the pentasulphide, or golden sulphide, in coloring rubber goods; the antimonate in coloring glass yellow; vitreous antimony sulphide made by roasting antimony sulphide, then fusing the product with fresh antimony sulphide, is also used to tint glass yellow, and for a like purpose with porcelain. The chromate, under the name of "Naples yellow," is used as a fine artist's color. Naples yellow and some of the oxides are used as ceramic colors.

Antimony in the form of metal and oxide is used in making flint glass. About 1½ pounds of each per ton of "batch" is used.

*New Potash Discoveries.*—As the United States has been purchasing one-sixth of Germany's annual export of about \$35,000,000 worth of potash, the following report from Consul Talbot J. Albert, of Brunswick, will be of interest:

Hitherto it has been believed that Germany was the only country in the world where deposits of potassium salts existed, and had therefore a safe monopoly of them. Now, however, comes the startling news in the press of the discovery of potassium deposits in other countries. The *Brunswick Landes-Zeitung* says:

It is already an established fact that potassium salts occur in Galatia, Hungary, Tyrol, Russia, Holland, Florida and Persia. (The United States Geological Survey has not yet been able to locate the reported Florida deposits, concerning which several press notices have appeared.—B. of M.) The latest German discoveries are located in Alsace, close to the French boundary, and the potassium deposits there will probably extend across into France, as has been the case with the salt wells.

There still comes the surprising information that potassium salts have been found in the vast Empire of China. Although this news might at first seem incredible, it has been a well-known fact for some time, but kept secret by interested parties. Samples of these salts have been tested by a chemist connected with the Potassium Mining Syndicate, and the results have given a large percentage of chloride of potassium (Chlorokali-um).

All particulars, especially the localities of the discoveries in China, are naturally withheld by the combine. Should the mining of the potassium salts in China be successful, the western part of America will first come in question as a consumer. The salts could be delivered there very cheaply, as the wages of labor in Chinese mines is one-tenth of those in German mines, and especially the cheap ocean freight to the west coast of America will be an important factor.

*World's Sugar Crop.*—Consul-General Henry W. Diederich, of Antwerp, has prepared, under date of January 8th, the following review of the sugar production of the world for the 1909-'10 season:

As usual, various approximate beet-sugar crop estimates have been issued from time to time during recent months, by sugar factories and others interested in the production of sugar in Europe. The unusually wet and cold summer had proved very unfavorable to the development of sugar beets in most countries of Europe, but fairer skies in autumn helped considerably to improve both the quality and quantity of beets. However, the sugar contents fall much behind that of last season, amounting in Belgium to only 15 per cent., whereas in 1908 they reached the high average of 17 per cent.

The season is completely finished in Belgium, and practically so in the other countries, so that only slight variations, one way or the other, in the present approximate estimates of the beet-sugar crop, may be looked for when the final actual results are recorded at the end of the year on August 31, 1910. The International Association for Statistics, therefore, after having issued approximate statements of the sugar crop in October and November, has just completed its third and last report, at the end of December, after having made another very careful inquiry, and now publishes the following total results for 1909-'10 of the sugar-beet fields in Europe:

Country.	Beets.	Sugar.
Germany.....	12,846,560	1,985,460
Austria.....	8,100,200	1,259,100
France.....	6,354,900	807,500
Russia.....	6,888,860	1,144,150
Belgium.....	1,765,000	240,900
Holland.....	1,291,000	175,500
Sweden.....	894,350	125,300
Denmark.....	488,000	65,000
Italy <sup>1</sup> .....	1,000,000	116,000
Spain <sup>1</sup> .....	830,000	99,300
Roumania <sup>1</sup> .....	203,000	28,000
Servia <sup>1</sup> .....	63,000	8,400
Switzerland <sup>1</sup> .....	25,000	3,100
Bulgaria <sup>1</sup> .....	28,000	3,300
Total.....	40,777,870	6,061,010

Mr. F. O. Licht, the veteran German sugar statistician, whose work I have closely followed for a number of years and found as unerring as human effort can attain, publishes the following crop estimates, based upon his own close observations and modified by his experience of a lifetime:

Country.	1909-'10.	1908-'09.	1907-'08.
	Tons.	Tons.	Tons.
Germany.....	2,005,000	2,066,779	2,116,595
Austria.....	1,250,000	1,370,453	1,397,260
France.....	810,000	783,904	711,541
Russia.....	1,175,000	1,274,659	1,415,115
Belgium.....	240,000	256,442	230,797
Holland.....	180,000	214,343	175,184
Sweden.....	125,000	133,383	109,012
Denmark.....	65,000	66,298	52,661
Italy.....	116,000	165,312	135,965
Spain.....	100,000	119,387	123,523
Roumania.....	25,000	22,600	25,832
Others.....	18,000	15,955	16,357
Total.....	6,109,000	6,488,915	6,509,842

<sup>1</sup> Unofficial estimates of the other beet-sugar-producing countries in Europe which do not belong to the International Association.

Country.	1906-'07. Tons.	1905-'06. Tons.
Germany.....	2,225,021	2,403,805
Austria.....	1,315,686	1,478,737
France.....	740,291	1,065,469
Russia.....	1,458,823	987,474
Belgium.....	280,928	326,962
Holland.....	181,407	207,189
Sweden.....	157,956	125,300
Denmark.....	62,275	64,369
Italy.....	106,383	93,916
Spain.....	98,085	90,206
Roumania.....	32,000	31,444
Others.....	14,240	7,150
Total.....	6,673,095	6,888,021

(The later statistics issued by Licht on January 21st, according to Willett & Gray's bulletin, gives the 1909-'10 crop estimate at 6,185,000 tons, being 35,000 higher for Germany, 10,000 higher for Austria, 15,000 higher for France, 10,000 higher for Belgium, 20,000 higher for Holland, and 25,000 tons higher for Russia, with a less amount for "all others."—B. of M.)

As the first decade of this century has just come to its close it is interesting to study the following table and note what has been accomplished in Europe during that period (hectare=2.47 acres):

Season.	Area (hectares).	Beets.		Sugar.	
		Tons.	Pounds per acre.	Tons.	Pounds per acre.
1909-'10.....	1,832,590	40,496,720	20,003	6,109,000	3,009
1908-'09.....	1,808,158	41,270,021	20,704	6,488,905	3,252
1907-'08.....	1,872,419	42,510,724	20,303	6,509,842	3,116
1906-'07.....	1,821,473	45,275,316	21,440	6,673,095	3,270
1905-'06.....	1,871,229	48,267,128	23,003	6,888,021	3,294
1904-'05.....	1,610,800	31,962,027	17,695	6,667,980	2,583
1903-'04.....	1,755,692	40,311,209	20,479	5,860,991	2,999
1902-'03.....	1,786,964	38,732,557	19,326	5,530,961	2,792
1901-'02.....	1,962,685	49,546,329	22,511	6,722,051	3,057
1900-'01.....	1,842,142	42,466,828	20,550	5,970,070	2,869

## CANE SUGAR RESULTS.

It is extremely difficult at present, even approximately, to give the crop estimates of cane sugar which is being produced

	1909-'10. Tons.	1908-'09. Tons.	1907-'08. Tons.	1906-'07. Tons.
Cuba.....	1,800,000	1,514,000	963,000	1,431,000
Porto Rico.....	270,000	222,000	190,000	181,000
Haiti and Dominican Republic.....	60,000	75,000	54,000	58,000
Jamaica.....	7,000	5,000	13,000	14,000
Barbados.....	30,000	12,000	33,000	35,000
Trinidad.....	45,000	41,000	39,000	40,000
Martinique.....	36,000	38,000	38,000	38,000
Lesser Antilles.....	45,000	40,000	40,000	45,000
Antigua and St. Kitts.....	25,000	25,000	23,000	30,000
Guadeloupe.....	35,000	25,000	36,000	39,000
St. Croix.....	13,000	12,000	12,000	10,000
Brazil.....	275,000	280,000	195,000	250,000
Argentina.....	130,000	162,000	110,000	119,000
Peru.....	130,000	150,000	135,000	169,000
Venezuela.....	3,000	3,000	3,000	3,000
Demerara.....	100,000	116,000	99,000	116,000
Surinam.....	12,000	12,000	12,000	9,000
Central America.....	50,000	50,000	50,000	50,000
Mexico.....	130,000	115,000	113,000	105,000
Egypt.....	45,000	40,000	42,000	65,000
Natal.....	54,000	40,000	41,000	36,000
Mauritius.....	225,000	188,000	165,000	214,000
Reunion.....	45,000	39,000	39,000	43,000
Fiji Island.....	70,000	65,000	68,000	40,000
Formosa.....	160,000	121,000	71,000	65,000
Java.....	1,150,000	1,187,000	1,244,000	1,115,000
Other East Indies.....	2,120,000	1,927,000	2,141,000	2,450,000
Queensland.....	140,000	151,000	188,000	175,000
New South Wales.....	15,000	15,000	29,000	23,000
Philippines.....	115,000	108,000	132,000	111,000
Hawaii.....	475,000	448,000	486,000	383,000
Louisiana.....	330,000	320,000	330,000	230,000
American home-grown beet.....	420,000	386,000	455,000	435,000
Total.....	8,560,000	7,932,000	7,595,000	8,127,000

in many countries all over the globe outside of Europe, and which is in various stages of growth and maturity. No one can tell to-day what quantities of sugar will be garnered from the cane fields of the East and West Indies, the two leading cane-producing countries. But for all practical purposes the above estimates may be safely made.

Finally, what has become of the world's sugar crop during the past four years; how much of it was left at the end of each year, after satisfying the demands of trade? What the results are likely to be during the present year, ending August, 1910, may be learned from the following table, showing actual returns of the world's sugar trade since 1905:

	1909-'10. Tons.	1908-'09. Tons.	1907-'08. Tons.
Initial stock September 1st.....	1,650,000	2,002,000	2,014,000
Production of beet sugar.....	6,109,000	6,494,000	6,510,000
Production of cane sugar.....	8,500,000	7,932,000	7,610,000
Total.....	16,259,000	16,428,000	16,134,000
Balance on hand August 31st.....	1,600,000	1,650,000	2,002,000
World's consumption.....	14,659,000	14,788,000	14,132,000
	1906-'07. Tons.	1905-'06. Tons.	
Initial stock September 1st.....	1,810,000	1,767,000	
Production of beet sugar.....	6,173,000	6,888,000	
Production of cane sugar.....	8,127,000	7,610,000	
Total.....	16,110,000	15,774,000	
Balance on hand August 31st.....	2,014,000	1,809,000	
World's consumption.....	14,596,000	13,965,000	

Thus it will be seen that the production of beet sugar has steadily grown less during recent years, while that of the cane has increased to such an extent as not only to cover the shortage in beet sugar, but also to add to the market a sufficient quantity to supply the world's demand for sugar, with a limited surplus at the end of the season, scarcely enough to keep the world supplied for six weeks. It also may be interesting to learn the fact that of the average annual world's sugar crop, about two-thirds, or 10,000,000 tons are used in Europe, the United States, and Canada, while the other third is absorbed by the rest of the world.

*Production of Radium.*—AUSTRIA: Consul Will L. Lowrie, of Carlsbad, transmits the following translation of an article which recently appeared in the Vienna Neue Frei Presse concerning the production and sale of radium in Austria:

At the Ministry of Public Works many conferences have been held lately to discuss the place where radium may be sold and to arrange details of putting the mineral on the market. The quantity to be disposed of consists of the recent shipment from Joachimsthal which was sent for experimental purposes, and which has been examined to determine the amount of pure radium it may contain. Already it is certain that the ore sent from Joachimsthal will yield not less than the amount of pure radium expected—1 gram. As has been said, this will be sold and the price is fixed at 380 crowns (\$77.14) a milligram. Persons or institutions which contemplate purchasing radium may have their addresses noted at the Ministry of Public Works, and already, before the official selling has begun, many applications have been filed, not only from the Empire but also from foreign countries. Many hospitals are among the applicants. Special means for packing the radium have been adopted owing to the danger from the rays. Since this shipment from Joachimsthal, a like amount of radium has been produced at the Imperial factory located at that place. It is hinted that if the chemical works at Joachimsthal are carried on in an adequate manner a number of other extremely valuable radioactive substances beside radium, as actinium and ionium, may be obtained, which in some regards, as, for instance, in the power of throwing out rays, may surpass radium.



ENGLAND: The following information concerning the establishment of a factory in London for the manufacture of radium according to a secret process discovered by Sir William Ramsay is taken from a London newspaper:

It is claimed that by this process the production of radium will be reduced from nine months to six or seven weeks, and the British Radium Corporation has been formed for taking over the radium rights of the Trentwith mine at St. Ives, where the discovery of pitchblende ore was made (previously referred to in Consular and Trade Reports). The services of Sir William Ramsay have been retained by the corporation.

The total quantity of radium which has thus far been recovered for scientific use throughout the world is estimated not to exceed one-fourth of a pound. The total stock in the London Hospital is but about 16 $\frac{1}{4}$  milligrams.

A little while ago the pitchblende containing this wonderful element was actually regarded as a nuisance by the old miners of St. Ives, so that it was cast aside on the rubbish heap, a heap which grew to mountainous proportions, and from which to-day the company is obtaining tons of material.

*American Exposition at Berlin* POSTPONED FOR ONE YEAR: Special Agent Julien L. Brode writes from Berlin, under date of February 7th, on the progress and prospects of the forthcoming American exposition in the German Imperial capital, the date of which has been changed since this report was written to 1911:

It is announced that William C. Brumder, of Milwaukee, Wis., one of the proprietors of the Germania-Abend Post there, has been appointed by the Department of State as honorary commissioner-general to the American Exposition at Berlin. Four honorary commissioners have also been selected, namely, Herman A. Metz, until recently comptroller of the city of New York; John Ball Osborne, chief of Bureau of Trade Relations at Washington; Irwin M. Laughlin, secretary of the United States Embassy at Berlin, and Hugh Gordon Miller, an attorney of New York, who was New York Commissioner to the Jamestown Exposition at Norfolk.

Former Comptroller Metz, of New York City, chairman of the American executive committee of the Berlin Exposition, gave out the following statement on February 28th:

In view of the apparent opposition which has developed in Germany against the American Exposition to be held in Berlin during the coming summer, the American executive committee has decided upon a postponement until 1911.

The members of the executive committee, and the gentlemen who agreed to serve on the advisory and other committees, did so for the purpose of showing their good will toward Germany and German interests and to promote the commercial relations between the two countries and in anticipation of similar co-operation on the part of the commercial interests of Germany and for no other reason.

As apparently this is not entirely understood, the members of the executive committee are of the opinion that it might be advisable to make the exposition a German-American affair in which both countries should participate, and thus prove it is not intended to be an American industrial invasion. With this object in view the majority of the members of the executive committee will visit Berlin in the coming summer for the purpose of bringing about, if possible, such a German-American exposition, and the United States Government has been requested to continue the honorary commission which was appointed to represent it at the exposition this summer.

## OFFICIAL REGULATIONS AND RULINGS.

Only a few of the more important rulings are reported here. For others the reader is referred to the publications of the Board of Food and Drug Inspection and to Treasury Decisions.

### NOTICE OF JUDGMENT No. 147, FOOD AND DRUGS ACT.

#### *Adulteration and Misbranding of Lemon Extract.*

In accordance with the provisions of Section 4 of the Food

and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 10th day of November, 1908, in the District Court of the United States for the Eastern District of Virginia, in a prosecution by the United States against the Suffolk Drug and Extract Company, a corporation of Suffolk, Va., for violation of Section 2 of the aforesaid act in shipping and delivering for shipment from Virginia to North Carolina an adulterated and misbranded lemon extract, the said Suffolk Drug and Extract Company entered a plea of guilty and the Court imposed a fine of \$25.

The facts in the case were as follows:

On August 24, 1907, an inspector of the Department of Agriculture purchased from J. J. Medford, Oxford, North Carolina, a sample (I. S. No. 2094) of a food product labeled: "Pure Brand Extract Lemon. Artificial Coloring. Manufactured by Suffolk Drug & Extract Co., Inc., Suffolk, Va." The sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and the following results obtained and stated:

Alcohol by volume (per cent.)	44.00
Lemon oil (per cent.)	0.18
Citral	0.02
Solids	0.10
Color: artificial color declared.	

Lemon extract, or flavor, as recognized by reliable manufacturers and dealers, is the flavoring extract prepared from oil of lemon, or from lemon peel, or both, and contains not less than five per cent. by volume of oil of lemon. The analysis of the aforesaid sample disclosed that there was only 0.18 per cent. of oil of lemon in this article, hence it was adulterated within the meaning of Section 7 of the act in that an inferior extract, artificially colored in a manner whereby its inferiority was concealed, was substituted wholly for the genuine article which it purported to be, and was misbranded within the meaning of Section 8 of the act in that it was labeled "Extract Lemon," which statement was false, misleading and deceptive because it was not lemon extract, but a very poor imitation thereof.

It appearing from the aforesaid analysis that the article was adulterated and misbranded, the Secretary of Agriculture gave notice to J. J. Medford, the dealer from whom the sample was procured, and also to the Suffolk Drug and Extract Company, the manufacturer and shipper, and gave them an opportunity to be heard. The said company being the party solely responsible for the adulteration and misbranding of the article and failing to show any fault or error in the result of the aforesaid analysis, and it being determined that the article was adulterated and misbranded, on July 2, 1908, the said Secretary reported the facts and evidence (F. & D. No. 133) to the Attorney General, by whom they were referred to the United States Attorney for the Eastern District of Virginia, who presented the facts to the grand jury, by whom an indictment was duly returned against the said Suffolk Drug and Extract Company with the result hereinbefore stated.

JAMES WILSON,  
Secretary of Agriculture.

January 15, 1910.

### NOTICE OF JUDGMENT No. 152, FOOD AND DRUGS ACT.

#### *Adulteration and Misbranding of Pineapple and Lemon Extracts.*

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on June 8, 1909, in the District Court of the United States for the Southern Division of the Southern District of Alabama, in a prosecution by the United States against the Mobile Drug Company, a corporation of Mobile, Alabama, for two violations of Section 2 of the aforesaid act in shipping and delivering for shipment from Alabama to Mississippi adul-

terated and misbranded pineapple and lemon extracts, the said Mobile Drug Company entered a plea of guilty and the Court imposed upon it a fine of \$25.

The facts in the case were as follows:

On February 22, 1908, and March 13, 1908, an inspector of the Department of Agriculture purchased from Mrs. Sophia Fields, Escatawpa, Mississippi, and R. W. Fagan & Company, Waynesboro, Mississippi, respectively, samples (I. S. Nos. 5051 and 2126-a) of food products labeled, respectively: "Pure Concentrated Extract of Pineapple for Flavoring Ice Cream, Custards, Jellies, Pastry, etc. Mobile Drug Co., Mobile, Ala.," and "Concentrated Extract of Lemon. Guaranteed ——— June 30, 1906. Serial No. 6901. Mobile Drug Co., Mobile, Ala." The samples were analyzed in the Bureau of Chemistry of the United States Department of Agriculture and the following results obtained and stated:

I. S. No. 5051:	
Specific gravity.....	0.9447
Alcohol by volume (per cent.).....	45.40
Esters as ethyl butyrate (grams per 100 cc.)...	0.696
Coloring matter.....	Turnmeric
I. S. No. 2126-a:	
Specific gravity (15.5° C.).....	0.8748
Alcohol by volume (per cent.).....	73.28
Solids (grams per 100 cc.).....	0.21
Lemon oil by polarization (per cent.).....	3.22
Lemon oil by precipitation (per cent.).....	3.30
Color.....	Turnmeric

A flavoring extract, as recognized by reliable manufacturers and dealers, is a solution in ethyl alcohol of proper strength of the sapid and odorous principles derived from an aromatic plant, or parts of the plant, with or without its coloring matter, and conforms in name to the plant used in its preparation; and lemon extract, or flavor, as recognized by reliable manufacturers and dealers, is the flavoring extract prepared from oil of lemon, or from lemon peel, or both, and contains not less than five per cent. by volume of oil of lemon. The analysis of sample I. S. No. 5051 disclosed practically the total absence of the sapid and odorous principles of the pineapple, hence the article was adulterated within the meaning of Section 7 of the act in that an imitation extract, artificially colored in a manner whereby its inferiority was concealed, was substituted wholly for the pineapple extract which it purported to be, and was misbranded within the meaning of Section 8 of the act in that it was labeled "Pure Concentrated Extract of Pineapple," which statement was false, misleading and deceptive because it was not an extract of pineapple, but merely an imitation extract. The analysis of sample I. S. No. 2126-a disclosed the fact that it contained only 3.3 per cent. of oil of lemon and was artificially colored, hence the article was adulterated within the meaning of Section 7 of the act in that an inferior extract, artificially colored in a manner whereby its inferiority was concealed, was substituted wholly for the genuine product which it purported to be, and was misbranded within the meaning of Section 8 of the act in that it was labeled "Concentrated Extract of Lemon," which statement was false, misleading, and deceptive because it was not concentrated extract of lemon, but an inferior grade lemon extract, artificially colored in a manner whereby its inferiority was concealed.

It appearing from the aforesaid analyses that the articles were adulterated and misbranded, the Secretary of Agriculture gave notice to Mrs. Sophia Fields and R. W. Fagan & Company, the dealers from whom the samples were purchased, and also to the Mobile Drug Company, the manufacturer and shipper, and gave them an opportunity to be heard. The Mobile Drug Company being the party solely responsible for the adulteration and misbranding of the articles and failing to show any fault or error in the results of the aforesaid analyses and it being determined that the articles were adulterated

and misbranded, on January 6, 1909, and February 27, 1909, respectively, the said Secretary reported the facts and evidence (F. & D. Nos. 306 and 486) to the Attorney-General, by whom they were referred to the United States Attorney for the Southern District of Alabama, who filed an information against the Mobile Drug Company with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

January 15, 1910.

(Notice of Judgment No. 175, Food and Drugs Act.) *Adulteration of Water.*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 19th day of August, 1909, in the Police Court of the District of Columbia, judgment was entered in the case of the United States against Frank H. Finley, trading as F. H. Finley & Sons, a prosecution upon an information in substance charging said defendant with having sold and offered for sale in the District of Columbia 24 bottles of a liquid substance intended for use as drink by man, labeled "Diamond Distilled Water," which was adulterated in that it was injurious and deleterious to health and contained poisonous and deleterious ingredients, and consisted wholly or in part of filthy, decomposed, and putrid vegetable substances. The defendant pleaded not guilty to the above information, and the case was tried on August 4 and 5, 1909. After hearing the testimony and arguments of counsel, the court found the defendant guilty as alleged in the information and imposed upon him a fine of \$10.

The facts upon which the above prosecution was based were as follows:

An inspector of the United States Department of Agriculture purchased a sample of the water labeled as above described from F. H. Finley & Sons, 208 Massachusetts Avenue, N. E., Washington, D. C. This sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found to contain the colon group of organisms. The analysis having disclosed an adulteration of said water, F. H. Finley & Sons were duly notified of the results obtained, and were given an opportunity to be heard and were heard in regard to said adulteration. It appearing that there had been a violation of the act, the Secretary of Agriculture, on May 19, 1909, reported the facts to the Attorney-General. The case was then referred to the United States Attorney for the District of Columbia, who filed the above information, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 179, Food and Drugs Act.) *Adulteration and Misbranding of Cottonseed Feed Meal.*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 18th day of June, 1909, in the District Court of the United States for the Western District of North Carolina, judgment was rendered in the case of the United States v. 120 Sacks of Cottonseed Feed Meal, wherein a libel was under Section 10 of the aforesaid act, alleging in substance that 120 sacks of a product designated as cottonseed feed meal and labeled: "Creamo Brand Feed Meal. Manufactured by the Tennessee Fibre Co., Memphis, Tenn. Guaranteed Analysis—Protein 22%, Fat 5%, Crude Fibre 28%," which had been shipped from Memphis, Tenn., to Asheville, N. C., and there found in original unbroken packages, were misbranded in that the label on said sacks represents the product to contain protein 22 per cent., fat 5 per cent., crude fibre 28 per cent., when in truth and in fact but 17.73 per cent. of protein, 4.69 per cent. fat, and 25.04 per cent. crude fibre, and approximately 50 per cent. cottonseed

hulls were present in said product, and were adulterated in that the said contents were designated as cottonseed feed meal with intent to deceive and mislead the purchaser as to its quality.

The libel prayed process against all claimants to said feed meal, and seizure and condemnation of the same.

The Asheville Grocery Company appeared as respondent in the above proceedings, whereupon the court, after parties had agreed to make statements of their evidence, found for the libellant and rendered the following decree:

IN THE DISTRICT COURT OF THE UNITED STATES, WESTERN DISTRICT OF NORTH CAROLINA. AT ASHEVILLE.  
UNITED STATES OF AMERICA

120 SACKS OF COTTON SEED FEED MEAL. }  
U. S. }  
DECREE OF CONDEMNATION.

This cause coming on to be heard, and it appearing to the Court that upon the Libel filed herein, Warrant of Arrest was duly issued and served on the 7th day of June, 1909, and that by virtue of said Warrant, the Marshal has seized and now holds 116 sacks of Cotton Seed Feed Meal of the approximate value of \$200.00 the said 116 Sacks of Cotton Seed Feed Meal, having been seized from the premises and in the possession of the Asheville Grocery Co. a partnership formed and doing business in the city of Asheville, N. C., within the said District and that the said Cotton Seed Feed Meal is now in storage and in the custody of the said Marshal; and it appearing that the Asheville Grocery Co. the respondent herein the owners of the said 116 bags of Cotton Seed Feed Meal, so seized were duly warned to appear herein and that due and legal notice and proclamation was given to all persons having or claiming to have any right, title or interest therein or in or to said property, to appear and answer said libel, and that said Asheville Grocery Co. have so appeared; the libellant and respondent each making a statement to the Court of their evidence and agreeing in open court to submit the same to the court and the court being now fully advised in the premises, finds for the libellant and finds that the said 116 sacks of Cotton Seed Feed Meal contains articles of food and that the said sacks are misbranded within the meaning of the Act of Congress of June 30, 1906, the same having been transported in interstate commerce from the City of Memphis, Tenn., consigned to the Asheville Grocery Co., at Asheville, N. C., being all of such consignment found in original unbroken packages, that is, the Court finds that the said articles of feed are misbranded in violation of the said Act of Congress in that said sacks and each of them contain protein 18.73 per cent., fat 4.69 per cent., crude fibre 25.04 per cent. and contain approximately 50 per cent. hulls, and that the said articles of feed were transported in interstate commerce and consigned and delivered to the claimant aforesaid, Wholesale dealers at Asheville, N. C.

The Court further finds that the articles of feed contained in said 116 sacks of Cotton Seed Feed Meal is not adulterated, poisonous or deleterious, but that the violation of said Act of Congress is in the misbranding of the said sacks and that the same were consigned only to a wholesale dealer and not sold to the public for consumption.

Wherefore, it is Ordered, adjudged and decreed by the court that the said 116 sacks of Cotton Seed Feed Meal with the contents as aforesaid, be and they are hereby declared to be misbranded in violation of the Act of June 30th, 1906, as is charged in said libel, and it is further ordered that the said 116 sacks of Cotton Seed Feed Meal, with the contents as aforesaid, be, and they hereby are condemned and forfeited as provided for in the said Act of June 30, 1906. It is provided, however, that upon the payment of all the cost in the proceeding herein including all Court, Clerk's and Marshal's costs and costs of hauling, storage, watchmen and all other costs incident to or contracted in this proceeding, and the execution and delivery

by the said Asheville Grocery Co. to the libellant of a good and sufficient bond in the penalty of \$250.00, conditioned that the said sacks of Cotton Seed Feed Meal, with the contents as aforesaid shall not be sold, or otherwise disposed of, contrary to the provisions of the said Act of June 30, 1906, or to the laws of any state, territory, district, or insular possession, that the said Marshal shall redeliver the said 116 sacks of Cotton Seed Feed Meal with such of their contents as they now contain or may contain at the time of such redelivery to the Asheville Grocery Co. in lieu of the retention and destruction thereof; The Clerk of this court will attach the costs in accordance with this order and furnish a copy thereof to claimants.

This June 18, 1909.

WM. T. NEWMAN,  
U. S. Judge presiding.

We consent to this decree:

THOS. J. RICKMAN, *Atty. for claimant.*  
A. L. COBLE, *Asst. U. S. Atty.*

The facts preceding the filing of the above libel were as follows:

On or about June 4, 1909, an inspector of the United States Department of Agriculture found in the possession of the Asheville Grocery Company, in original unbroken packages, 120 sacks of product labeled as above described, which had been sold, invoiced, and shipped as Cotton Seed Feed Meal to the said company by the Tennessee Fibre Company, of Memphis, Tenn. A sample taken from the above consignment was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found to contain protein 18.73 per cent., fat 4.69 per cent., crude fibre 25.04 per cent., and hulls, approximately, 50 per cent. The misbranding and adulteration disclosed by this analysis was reported by the Secretary of Agriculture, on June 5, 1909, to the United States Attorney for the Western District of North Carolina, who filed the above libel, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 180, Food and Drugs Act.) *Misbranding of a Drug—"Gowan's Pneumonia Cure."*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on December 16, 1908, in the District Court of the United States for the Northern District of Illinois, a judgment was rendered in the case of the United States *v.* Gowan Medical Company, a corporation organized and existing under the laws of the State of North Carolina and transacting business through a branch office at Chicago, Ill., a prosecution upon an information in substance charging said defendant corporation with having delivered to the Baltimore and Ohio Railroad Company, at Chicago, Ill., for shipment to Washington, D. C., four cases of a certain drug called "Gowan's Pneumonia Cure," which was misbranded in the following particulars, *viz:*

1. On a green circular enclosed in the carton and surrounding each of the bottles containing this drug, and thereby made a part of the labels descriptive of the said preparation, occurred this statement: "It is entirely different from any other remedy containing new principles never before applied; consequently, it cannot be substituted," which said statement was then and there false and misleading in this, that all the ingredients in said preparation were and are well and commonly known and are constantly applied, singly or in combination, in the very manner directed by the instructions accompanying this preparation, and commonly used for the affections of the lungs, throat, and other portions of the body similarly affected.

2. On a green circular enclosed in the carton and surrounding each of the bottles containing this drug, and thereby made a part of the labels descriptive of said preparation, occurred



this statement: "Supplies an easily absorbed food for the lungs that quickly effects a permanent cure;" which statement was false and misleading in this, that there is no such thing as a food for the lungs separate and apart from a food that nourishes the whole body.

3. On a white circular also enclosed in the carton and surrounding each of the bottles containing the drug, and thereby made a part of the labels descriptive of said preparation, occurred this statement: "It was endorsed and advertisement accepted by the *American Medical Journal*, as a valuable therapeutic agent;" which statement was false and misleading in this, that the said preparation was never advertised in the *American Medical Journal* and was never endorsed by the said *American Medical Journal*.

The information charged a further misbranding in that the labels printed upon the cartons containing the bottles filled with this preparation did not bear a statement of the quantity of opium contained in said preparation in a manner that could be easily read by the purchaser; but the statement of the amount of opium contained therein was printed in inconspicuous type in such an inconspicuous place that the proper notice of the poisonous contents of said preparation was not easily conveyed to the purchaser or person to whom it might be transferred.

On the aforesaid date, the defendant pleaded guilty to the above information and was fined \$200. The facts on which the prosecution was based were as follows:

On November 22, 1907, an inspector of the United States Department of Agriculture purchased from the Washington Wholesale Drug Exchange a sample of a drug preparation labeled and branded as above described, which had been shipped to said Exchange by the Gowan Medical Company from Chicago, Ill., on or about November 18, 1907. This sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and was found to consist of stearin, lard, turpentine, camphor, phenol, quinine sulphate, opium, and a trace of quinine alkaloid. The analysis having disclosed a misbranding of the drug, the said Washington Wholesale Drug Exchange and the said Gowan Medical Company were duly notified of the charges and were given an opportunity to be heard and were heard in regard to said misbranding. It appearing that there had been a violation of the act, the Secretary of Agriculture, on May 28, 1908, reported the facts to the Attorney-General. The case was then referred to the United States Attorney for the Northern District of Illinois, who filed the above information, with the result hereinbefore stated.

JAMES WILSON,  
Secretary of Agriculture.

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 181, Food and Drugs Act.) *Misbranding of a Drug—"Eyelin."*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 21st day of December, 1908, in the District Court of the United States for the Northern District of Illinois, a judgment was rendered in the case of the United States against the Eyelin Company, a corporation of Chicago, Ill., a prosecution upon an information in substance charging said defendant corporation with having delivered to the United States post-office at Chicago, Ill., for shipment to Washington, D. C., a quantity of a drug preparation contained in a circular tin box, upon one side of which were printed the following words:

One Dollar Repairs and Rejuvenates  
Trade Mark EYELIN Registered  
The Eye and Sight  
The EYELIN CO., Chicago, U. S. A.

and upon the other side of which were printed directions for the use of said drug, said box being surrounded by a circular

entitled: "How to Use Eyelin and Your Eyes," which said tin box and surrounding circular were placed in a blue pasteboard box, upon the front of which were placed the following printed words:

Reshapes and Rejuvenates,  
Trade Mark EYELIN Registered,  
The Eye and Sight.

which said drug was misbranded in the following particulars:

(a) The label printed upon one face of the tin box containing said drug contained this statement: "Repairs and Rejuvenates the Eye and Sight," which said statement was false and misleading in this, that the perfumed vaseline enclosed in the circular tin box aforesaid, and constituting said preparation, had no properties capable of repairing the eye and the sight; and

(b) The label upon the blue pasteboard box in which the circular tin box containing the drug and the circular were placed contained this statement: "Reshapes and Rejuvenates the Eye and Sight," which statement was false and misleading in this, that the perfumed vaseline enclosed in the said tin box, constituting the preparation, had no properties capable of reshaping and rejuvenating the eye and sight.

On December 16, 1908, the defendant pleaded guilty to the information and the court imposed upon it a fine of \$10.

The facts upon which the above prosecution was based were as follows:

On or about February 13, 1908, an inspector of the United States Department of Agriculture purchased from the Eyelin Company, No. 1403 Washington Boulevard, Chicago, Ill., a box of the drug preparation heretofore described, the same being delivered to him at Washington, D. C., through the United States mail. This sample was analyzed in the Bureau of Chemistry, United States Department of Agriculture, and found to consist essentially of perfumed or flavored vaseline, wherefore it was deemed misbranded, and the said Eyelin Company was duly notified of the charge and given an opportunity to be heard, and was heard in regard to said misbranding.

It appearing that there had been a violation of the act, the facts were reported to the Attorney-General on June 25, 1908, by the Secretary of Agriculture. The case was referred to the United States Attorney for the Northern District of Illinois, who filed an information against the Eyelin Company, with the result hereinbefore stated.

JAMES WILSON,  
Secretary of Agriculture.

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 182, Food and Drugs Act.) *Misbranding of a Drug—"Bromo Febrin."*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 29th day of October, 1909, in the District Court of the United States for the District of Maryland, judgment was rendered in the case of the United States v. William H. Smaw, trading as W. H. Smaw & Company, a prosecution upon an information in substance charging said defendant with having shipped from Baltimore, Md., to Detroit, Mich., one dozen packages of a drug called "Bromo Febrin," which was misbranded in this, that the packages containing the same failed to bear a statement of the quantity or proportion of acetanilid contained therein; and which was further misbranded in that said packages bore the following statement: "Each Powder contains 4 Grains of Acetanilid," which said statement was false and misleading for the reason that said powders contained more than 4 grains of acetanilid, viz., nearly 6 grains; and which was further misbranded in this, that said packages bore the statement "Sure Cure for Headache and Neuralgia," which statement was then and there false and misleading because the article in said packages

was not a sure cure for headache and neuralgia; and which was further misbranded in this, that said packages bore this statement "Permanent in Results," which statement was false and misleading for the reason that the article contained therein was not permanent in results; and which was further misbranded in this, that the packages containing the same bore this statement "It is Absolutely Safe," which said statement was false and misleading because said drug was not absolutely safe.

The defendant pleaded guilty to the information on the aforesaid date, and the court imposed a fine upon him of \$20.

The facts on which the above prosecution was based were as follows:

On or about February 1, 1909, an inspector of the United States Department of Agriculture purchased from the Michigan Drug Company, of Detroit, Mich., a sample of the drug heretofore described, which was contained in a consignment shipped to said dealers from Baltimore, Md., by William H. Smaw, trading as W. H. Smaw & Company. This sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture, and each powder found to contain nearly 6 grains of acetanilid. The analysis having disclosed a misbranding of the drug, the Michigan Drug Company, and the said William H. Smaw, were duly notified thereof and were given an opportunity to be heard, and were heard in regard to said misbranding.

It appearing that there had been a violation of the act, the Secretary of Agriculture, on July 31, 1909, reported the facts to the Attorney-General. The case was thereupon referred to the United States Attorney for the district of Maryland, who filed an information against the said William H. Smaw, with the result hereinbefore stated.

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 183, Food and Drugs Act.) *Adulteration and Misbranding of Powdered Colocynth.*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 7th day of October, 1909, in the District Court of the United States for the District of Maryland, judgment was rendered in the case of the United States *v.* Gilpin, Langdon & Company, Inc., a prosecution upon an information in substance charging said defendant corporation with having shipped from Baltimore, Md., to Cincinnati Ohio, 3 pounds of a certain drug, which was then and there adulterated, in that it was then and there sold under a name, to wit, "Powdered Colocynth," recognized in the United States Pharmacopoeia and National Formulary, and then and there differed from the standard of strength, quality, and purity as determined by the test laid down therein, in this, that the standard of strength, quality, and purity as determined by said test requires that in colocynth ready for use the seeds should be separated and rejected, whereas, the colocynth shipped as aforesaid contained a mixture of pulp and seeds; and which said drug was misbranded in this, that the packages containing the same then and there bore a statement regarding the ingredients and the substances contained therein which was false and misleading for the reason that it represented said drug as consisting of powdered colocynth, whereas, in truth and in fact, said contents consisted of powdered colocynth mixed with a quantity of seeds.

On the aforesaid date the defendant pleaded guilty to the information, and the court imposed upon it a fine of \$25.

The facts on which the above prosecution was based were as follows:

On or about August 11, 1908, an inspector of the United States Department of Agriculture purchased a sample of the drug heretofore described from Theodore Rosenthal, Eighth and

Vine streets, Cincinnati, Ohio, which sample was contained in a consignment of said drug shipped to said dealer from Baltimore, Md., by Gilpin, Langdon & Company. This sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found to consist of the entire fruit, pulp, and seeds ground. The analysis having disclosed an adulteration and a misbranding of the drug, the said Theodore Rosenthal and the said Gilpin, Langdon & Company were duly notified of said charges, and were given an opportunity to be heard, and were heard, in regard to said adulteration and misbranding; whereupon, it having appeared that there had been a violation of the act, the Secretary of Agriculture, on July 28, 1909, reported the facts to the Attorney-General; the case was then referred to the United States Attorney for the District of Maryland, who filed an information against the said Gilpin, Langdon & Company, Inc., with the results hereinbefore stated.

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., January 28, 1910.

(Notice of Judgment No. 184, Food and Drugs Act.) *Misbranding of a Drug—"Radol."*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on February 3, 1909, and October 1, 1909, respectively, judgments were rendered in two cases of the United States against Dennis Rupert Dupuis, both prosecutions upon informations identical in terms except as to the dates of the shipments alleged. The first information, in one count thereof, in substance charged the defendant with having shipped from St. Louis, Mo., to Washington, D. C., a certain bottle then and there labeled "This bottle contains Radol (Registered Trade Mark), a radium impregnated fluid prepared according to the formula and under the supervision of Dr. Rupert Wells, St. Louis, Missouri. This fluid is not expected to retain its radioactivity beyond forty days from the date of this label. For External use. Name, E. G. Henson. Address, Washington, D. C. Date Feb. 22, 1908. Directions: To be used as directed by letter. Signature, D. R. Wells, M.D. Keep this bottle in a dark cool place;" the contents of which said bottle were misbranded in that the statements upon the label were false and misleading for the reason that said bottle contained a liquid which was not radium impregnated and which had no radioactivity beyond that of ordinary water, and further that the name Dr. Rupert Wells was a false and fictitious name, and that said fluid was not prepared according to the formula of a Dr. Rupert Wells or under his supervision; and in the second count thereof charged said defendant with having shipped from St. Louis, Mo., to Washington, D. C., a certain bottle then and there labeled "This bottle contains Radol (Registered Trade Mark), a radium impregnated fluid prepared according to the formula and under the supervision of Dr. Rupert Wells of St. Louis, Missouri. This fluid is not expected to retain its radioactivity beyond forty days from date of this label. For internal use. Name, E. G. Henson. Address, Washington, D. C. Date, Feb. 22, 1908. Directions: Take one tablespoonful in a wine glass of water before each meal and at bed-time. Signature, D. R. Wells, M.D. Keep this bottle in a cool dark place;" the contents of which said bottle were misbranded in that the label was false and misleading in the following particulars: The said liquid was not radium impregnated and had no radioactivity, and further in that the name Dr. Rupert Wells was a false and fictitious name and that said fluid was not prepared according to the formula of a Dr. Rupert Wells, or under the supervision of a Dr. Rupert Wells, and which was further misbranded in that the said liquid contained approximately 6.99 per cent. of alcohol, and that the label upon said bottle did not state the proportion of alcohol

contained in said liquid or that the liquid contained any alcohol.

The defendant pleaded guilty to both informations and on the dates aforesaid was fined \$100 and \$50, respectively.

The facts upon which the prosecutions were based were as follows:

An inspector of the United States Department of Agriculture, upon two occasions, purchased samples of the drug heretofore described from Dennis Rupert Dupuis, St. Louis, Mo. The samples were analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found not to be radium impregnated liquids, not to have any radioactivity beyond that of ordinary water, and to contain approximately 6.99 per cent. of alcohol. The analyses having disclosed an apparent misbranding of the liquids, the said Dennis Rupert Dupuis was duly notified thereof in each case and given an opportunity to be heard, and was heard, in regard to said misbranding. Thereupon it appeared that there had been violations of the act, and the Secretary of Agriculture, on December 8, 1908, and April 23, 1909, reported the facts to the Attorney-General. The cases were referred to the United States Attorney for the Eastern District of Missouri, who filed the informations against the said Dennis Rupert Dupuis, with the results hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., February 7, 1910.

(Notice of Judgment No. 189, Food and Drugs Act.) *Adulteration and Misbranding of Vinegar.*—In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 27th day of August, 1909, in the District Court of the United States for the Eastern District of Michigan, in a prosecution by the United States against the Gordon Vinegar Company, a corporation of Pontiac, Mich., for violation of section of the aforesaid act in shipping and delivering for shipment from Michigan to Ohio an adulterated and misbranded vinegar, the said Gordon Vinegar Company entered a plea of *nolo contendere* and the court sentenced it to pay the cost of the case.

The facts in the case were as follows:

On February 18, 1909, an inspector of the Department of Agriculture purchased from the W. W. Harper Company, Zanesville, Ohio, a sample of a food product labeled: "Gordon Vinegar Co. 46. Apple Cider Vinegar. Fermented. Pontiac, Mich.," which was part of a shipment made by the Gordon Vinegar Company from Pontiac, Mich., to the said W. W. Harper Company on or about December 26, 1908. The sample was analyzed in the Bureau of Chemistry of the United States Department of Agriculture and following results obtained and stated:

Solids.....	1.91
Reducing sugar invert.....	1.16
Per cent. sugar in solids.....	60.8
Polarization, direct, temp. °C. 26.....	2.6
Polarization, invert, temp. °C. 26.....	-2.6
Ash.....	0.26
Alk. sol. ash (cc. N/10 acid per 100 cc.).....	29.1
Sol. phos. acid (mgs. per 100 cc.).....	1.5

Insol. phos. acid (mgs. per 100 cc.).....	11.1
Acid. as acetic (wines tartaric).....	4.64
Volatile acid, as acetic.....	4.64
Fixed acid, as maleic wines tartaric.....	0.0
Lead precipitate.....	Small.
Color, degrees, brewer's scale 0.5 in.....	4.0
Color removed by Fuller's earth (per cent.).....	65.0
Ash in solids (per cent.).....	13.9
Salicylates and benzoates.....	Negative
Ratio $\frac{P_2O_5}{P_2O_5 + H_2O}$ water sol. (per cent.).....	11.9

Vinegar, cider vinegar, apple vinegar, as recognized by reliable manufacturers and dealers, is the product made by the alcoholic and subsequent acetous fermentations of the juice of apples. The analysis of the aforesaid sample disclosed that it contained dilute acetic acid, or distilled vinegar, and a foreign material high in reducing sugars. Hence the article was adulterated within the meaning of Section 7 of the act in that a mixture of dilute acetic acid, or distilled vinegar, and a foreign material high in reducing sugars had been substituted wholly or in part for the vinegar which it purported to be, and was misbranded within the meaning of Section 8 of the act in that it was labeled "Apple Cider Vinegar," which statement was false, misleading, and deceptive because it was not an apple cider vinegar, but a mixture of dilute acetic acid, or distilled vinegar, and a foreign substance high in reducing sugars.

It appearing from the aforesaid analysis that the article was adulterated and misbranded, the Secretary of Agriculture gave notice to the W. W. Harper Company, the dealer from whom the sample was procured, and also to the Gordon Vinegar Company, the manufacturer and shipper, and gave them an opportunity to be heard. The Gordon Vinegar Company being the party solely responsible for the adulteration and misbranding of the article and failing to show any fault or error in the result of the aforesaid analysis, and it being determined that the article was adulterated and misbranded, on July 26, 1909, the said Secretary reported the facts and evidence to the Attorney-General, by whom they were referred to the United States Attorney for the Eastern District of Michigan, who filed an information against the Gordon Vinegar Company, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., February 7, 1910.

## CORRECTION.

My attention has been called to the fact that in my paper in the December number of THIS JOURNAL on the "Volumetric Estimation of Potassium" some error in reference occurred. On page 796 it was stated that the average of a number of results secured by Mr. W. A. Drushel was 104.2 per cent., and the individual results were given. This it proves is an error on my part; as a matter of fact the results of his Table I were secured by the use of the Adie and Wood method, hence should be excluded from the average. This makes a much better general showing for his method, and I am glad to take this occasion to rectify my mistake in the matter.

L. T. BOWSER.





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## ORIGINAL PAPERS.

### LABORATORY TESTS OF LUBRICANTS—INTERPRETATION OF ANALYSES.

By P. H. CONRADSON.<sup>1</sup>

Received March 14, 1910.

To make complete tests of lubricants, oils and greases requires a great deal of expert knowledge and experience to enable the chemist or engineer to interpret correctly the results obtained. This point will be clearer perhaps, if one considers the various classes of machinery to be lubricated, from the light spindles in cotton mills to the heavy rolls in the iron and steel mills; the fast running shaft or journals in a dynamo, to the slow heavy shaft in an ocean steamer or war ship, and the numerous classes of machinery in shops, the electric motors on street cars, the steam locomotives, the railroad cars, the steam turbine, automobiles, air compressors, steam cylinders, and so on, too long a list to enumerate, and if we consider that these machines are to be lubricated under all kinds of conditions as to weather changes, high and low temperatures, and service requirements, we readily will appreciate the wide scope "Lubricants and Lubrication" involves.

The method or methods of applying the oil to the parts to be lubricated plays a very important part

in connection with the proper interpretation of lubricating oil analyses; the conditions of the bearing surface, composition of the journal and bearings, etc.

An oil that would give satisfaction when applied direct to the journal by means of soaked waste, might fail altogether if the wick method of feeding the oil was used, likewise a sight-feed cup with wide enough orifice might give satisfaction, while a gravity feed through a long small bored pipe, might give very unsatisfactory results; or in other words the chemist or oil expert to interpret the results from laboratory tests of lubricating oils must be familiar with the particular kind of machines to be lubricated, the service conditions and requirements, and method of applying the oil, before he can give a qualified opinion as to the real adaptability of the lubricant, or comparative merits of two oils intended for the same service.

The value of physical and chemical tests of iron and steel used in construction work of all kinds and how to interpret the results obtained in laboratories is well known, likewise we must consider the laboratory tests of lubricants from a technical and practical point of view somewhat in the same light.

In making a complete investigation of the real or comparative value of a lubricating oil with another oil, we have then to consider the kind of machine to be lubricated, the service requirements and conditions, and the methods of applying the lubricant to the machine, and make the chemical and physical laboratory tests accordingly.

Generally speaking, the chemical tests, as made, are very inadequate, as are also the physical tests, especially frictional tests on oil-testing machines, unless the machines are constructed in such a way that the actual conditions can be approximately reproduced. For instance, in testing a spindle oil, the testing machine should be run practically at the same load and speed as the spindles are in actual service. In testing railway car and coach oils, the machine should have approximately the same size journal and bearing as would be found in actual railway car journals. The same is also true as regards speed, load and the application of the lubricant.

While many valuable conclusions may be drawn from properly conducted laboratory tests, those of the greatest practical value come from a close observation of the lubricant in actual service, and we can base our laboratory investigations on the results obtained, especially in comparing different oils intended for the same work. To bring out the point more

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clearly, let us consider an air compressor, such as is used on street cars and electric locomotives. As is well known, these compressors are not water-cooled or even air-cooled. It is not difficult to get an oil that will lubricate the compressor cylinder, but it is difficult to find an oil that will not carbonize at the high temperature, often  $450$  to  $460^{\circ}$  F. in the street-car compressor, and  $550^{\circ}$  to  $560^{\circ}$  F. in the electric locomotive air compressor.

of a suitable oil for such service, and to make a proper laboratory investigation and test of an air-compressor oil, it would be necessary to have an air compressor and test the oil as near as possible under actual service conditions.

Again, we may consider a steam turbine and suitable oils for its lubrication. Ordinary laboratory tests, both chemical and physical, such as are generally used in this country, do not bring out the essential

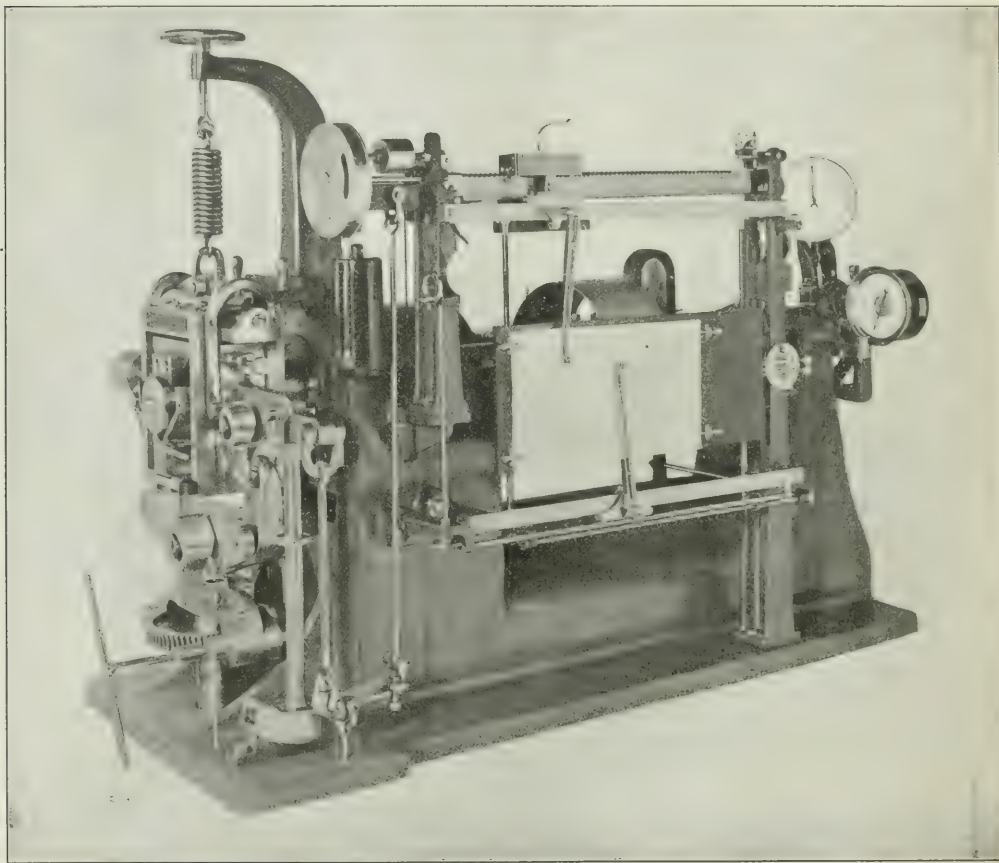


Fig 1

The difficulty lies in the fact that as the compressed air passes through the outlet ports and check valves in the compressor heads, there is a very rapid increase in the temperature. The small amount of oil that goes with the compressed air, if not of the best or suitable quality, will then begin to carbonize and cause trouble by forming heavy carbonaceous deposits on the check valves. Now, an ordinary oil-testing machine cannot bring out the essential requirements

qualities of a suitable turbine oil, because the service requirements and conditions are so entirely different from the general run of machinery, that special tests must be made. Therefore, from a practical point of view, to develop the essential qualities of turbine oils, it is necessary that the service conditions and requirements should be studied first, laboratory tests then being made in accordance therewith as far as practicable.



To illustrate, we consider a steam turbine of the Curtis type, where the oil is forced under high pressure to the step-bearing and then returned to the oil tank. At first this might be a very small matter, but in actual practice and experience it is not, for the following reasons: In the first place, leakage of steam occurs in most of these steam turbines as now constructed; this steam condenses, becomes mixed or churned in with the oil, and if the oil is not of the proper kind, it becomes emulsified. The emulsified oil gradually becomes thicker, and as the same circulating system is used for the rest of the machine, the emulsified oil often causes considerable trouble. Then again, we often find that the amount of oil used in the oil-circulating system is entirely too small in quantity, so the oil has to pass through the turbine many times during the hour, in the twenty-four hours, and from week to week. This imposes a severe service requirement on the oil, which gradually becomes polymerized and oxidized, developing petroleum acids. If sulphur compounds are present to any extent, they become gradually oxidized and besides causing corrosion may also cause a great deal of trouble from formation of asphaltic and tarry matter, which would clog the filters and orifices through which the oil has to pass. From a practical point of view, therefore, the laboratory tests of turbine oils should be considered along these lines. The same may be said of all lubricating oils intended for use in oil-circulating systems, which are now so largely used in stationary power plants, shops, and mills, war vessels, steamships, etc.

It is a generally accepted idea that if the oil is adapted to the load and speed, the lower the viscosity the better lubricant it will be. This, to my mind, holds good only where the service conditions are uniform, and where the method of applying the oil to the bearing and journal is a positive one, such as in gravity or pressure-pump systems. Where the climatic changes are great, as on railroads, this will not hold good.

The load and speed of the railroad trains are the same during the summer and winter, and as is well known, the practice in this country is to convey the oil to the journals by means of oil-soaked waste. A satisfactory thin winter oil with a low cold test and low viscosity, containing sufficient lubricating capacity to keep the journal and bearing apart, would not be suitable during the hot season, not because it has not the adequate sustaining power, but because of the method of applying it to the surfaces to be lubricated, making it necessary to use a much thicker oil than is theoretically required.

Therefore, to make laboratory tests of the relative lubricating values of oils considered from a practical standpoint and to draw correct conclusions from the results obtained, we must consider the kind of machine or machines to be lubricated; the speed and the load;

the composition of the metal bearing; whether the journals are iron or hard steel; the method of applying the lubricant, either with wick feed, soaked waste, sight-feed cups, flooded bearing or continuous oil-circulating system; the actual service requirements and climatic conditions. We must make complete chemical and physical tests as near as possible in accordance with these conditions. I might with propriety state that one oil cannot be considered a better lubricant than another oil unless the service conditions and requirements are specified and fully understood and the laboratory tests made in accordance therewith.

I have spoken of the importance of adequate chemical tests in connection with physical and frictional tests. The following tests are therefore useful. While in some cases it is not necessary to subject the oil to all these tests, they are of great importance in connection with special or unusual service requirements and conditions.

#### CHEMICAL TESTS.

Flash point	Evaporating tests, a given time
Burning point.	at 200° to 300° F. to study percentage of volatile and behavior of residues in 88° gasoline tests and acidity.
Gravity.	Heat tests, in air bath blowing air over the oil at 425° F. and 540° F. Examination of residue.
Color.	Emulsifying tests, to determine adaptability of the oil, say in turbine service.
Odor.	Tar and coke-forming substances present before and after heat test.
Purity.	Oxidation or gumming tests.
Gasoline tests, before and after flash.	Superheated steam tests.
Cloud test	Carbonizing test in connection with air compressor (not water-cooled) automobile gas-engine lubrication.
Cold test	Capillarity or wick tests.
Viscosity.	
Microscopic test for carbonaceous matter in suspension.	
Saponifiable fats.	
Free fatty acids.	
Petroleum acids.	
Sulphuric acids.	
Chemicals from imperfect refining.	
Sulphur-lamp tests and in wick.	
Maumené test.	
Iodine test.	

I will now consider the various tests and their importance.

#### *First and Second, Flash Point and Burning Point.*—

This test indicates the temperature at which the more volatile elements present in the oil begin to go off to such an extent as to give a flash when a small flame is moved over and near the surface of the heated oil; the so-called open-cup method is generally used, and in connection with this test, the heat is continued till the oil begins to burn, when the flame test is made.

A too low flash and fire test may be objectionable on account of danger from fire; besides, too large a loss from evaporation, under given service conditions, in connection with the viscosity, congealing point or cold test and gravity, the flash and fire test also enables the analyst to form an idea of the source of the petroleum.

*Third, Specific Gravity.*—The gravity enables the analyst in many cases to form an idea whether the oil is a Pennsylvania, Virginia or western oil, the latter generally having a much higher gravity.

*Fourth, Color.*—While not of much importance, other things being equal, an oil with a lighter color

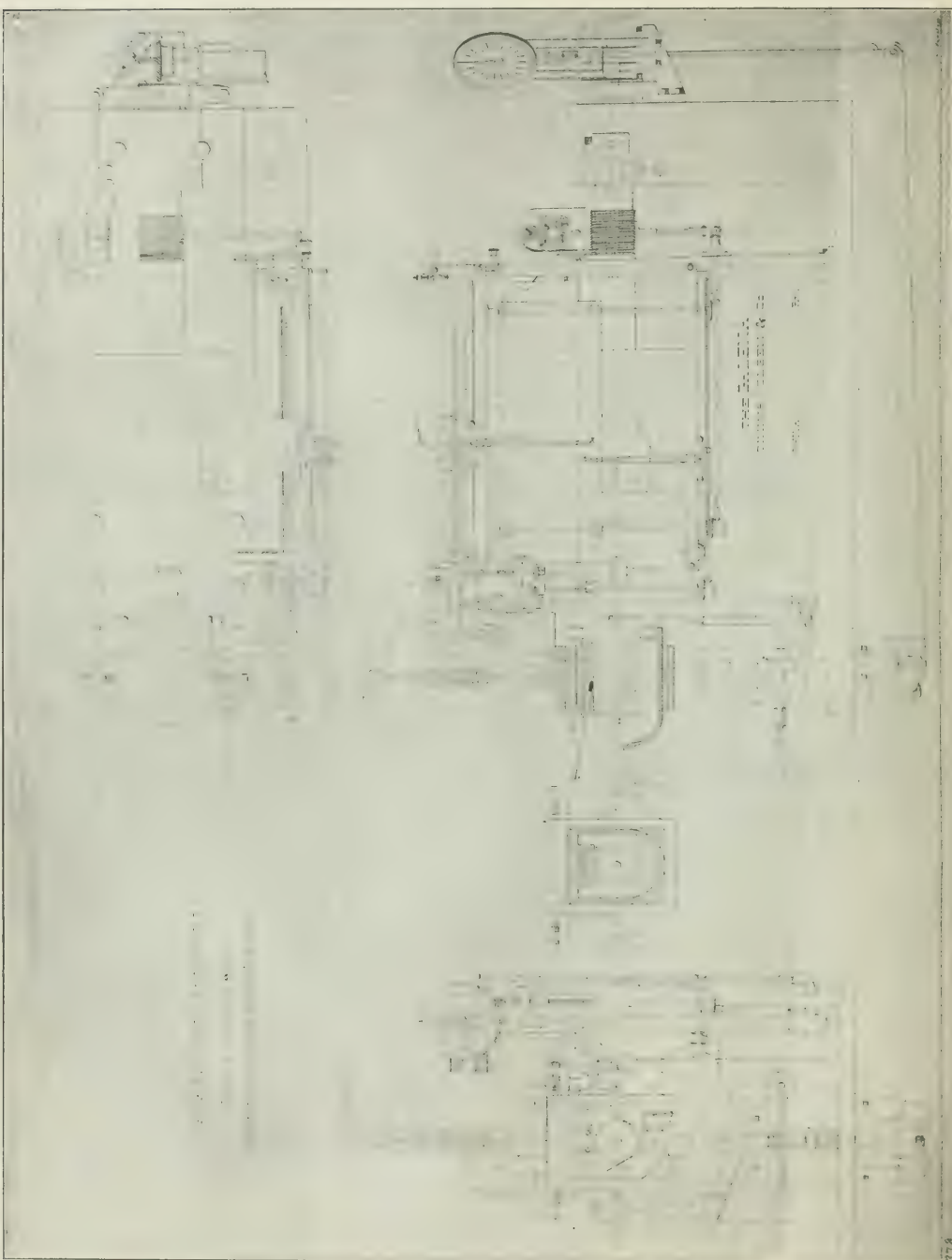


Fig. 2.—Galena signal oil testing machine.

or pleasing appearance is oftentimes preferred to a very dark or black colored oil.

*Fifth, Odor.*—At times aids in detecting the kind and quality of fat oils in compounded oils.

*Sixth, Purity.*—Freedom from water, matters in suspension, whether clear or turbid, etc.

*Seventh, Gasoline Tests.*—This test tells you if water or other foreign matters are present, tar and asphaltic matter, and if the oil gives a clear solution with 88° gasoline before it is heated to take the burning point, but gives a precipitate with 88° gasoline after said test; this indicates petroleum compounds which are readily acted upon by heat, and such an oil in comparison with another oil, other things being equal, would not have the same lubricating value.

*Eighth, Cloud Test* of a lubricating oil is sometimes of value in determining the amount of paraffines present and the behavior of the oil in chilling down to a temperature above congealing point.

*Ninth, Cold Test* (Congealing point, Melting point).—This test together with the viscosity of the oil in comparative tests is of much importance in connection with the service utility of the oil and should be given careful consideration.

The method used in determining the cold test and melting point, as well as getting at the comparative fluidity or sluggishness at temperatures lower than 70° F., is generally not considered as it should be. To illustrate: A valve or cylinder oil, if the cold test was taken by the so-called P. R. R. method (that is, the oil was frozen direct in ice mixture, and then stirred by the thermometer till it began to flow when the bottle is inverted), might show a cold test of 40° F., and if no further observation was taken one would have no idea of the fluidity of 60° to 70° F.; that is, the cold test in the report would give 40° F., but in reality the oil at 60° F. would be so sluggish that it would hardly feed through the narrow-bore feed-pipe to the steam chest and cylinders, and unless the analyst knows for a fact that the engineer has his pipe covered or warmed in some way, trouble may arise, the oil be condemned, and still the oil might be of the best and purest quality.

Again if the congealing point is taken by the S. O. Co.'s method (that is, the oil in the bottle with its thermometer inserted is put into a cooling box, gradually cooled till the oil just ceases to flow when the bottle is inverted, or still better, lifting up the thermometer stem from time to time and noting when the oil hardly flows from the stem), but without further observations this method like the P. R. R. does not tell all.

The rate of cooling or chilling, the time the oil remains in the chilling or cold test box, plays an important part in proper interpretation of the comparative value of the oil in actual service. Much more

could be said on this point, but the above allusion may be sufficient.

*Tenth, Viscosity.*—This test is the bugbear of the oil tester: it may mean so much and it may mean so little. Certainly in my line of work in connection with the cold test and flash point, we might have a good idea of the quality and adaptability of the oil with the aid of a good viscosimeter.

As an adjunct to other tests, and a careful study and knowledge of the service requirements, I have found the viscosity tests of the utmost value; in fact, from my knowledge of all the analytical data, with the aid of the viscosimeter, I can pretty near foretell the comparative friction under given conditions between two oils.

*Eleventh, Microscopic Tests.*—In testing dark-colored oils, heavy machine oils, and cylinder oils, it is well to put a few drops on a slide and examine under the microscope—one may find carbonaceous matter in suspension; and paraffine crystals if present at ordinary temperatures will disappear on warming the oil, and other foreign matters held in suspension will be brought out.

Certainly an oil, other things being equal, that is free or practically so from carbonaceous specks or flakes is superior to an oil containing these in some quantity.

*Twelfth, Saponifiable Fats.*—I will not enter into a discussion of the methods to determine these, but merely point out that two cylinder oils, one containing 30 per cent. of fat oil and the other only say 5 to 10 per cent. of fat oil, other things being equal, while not of the same intrinsic commercial value, may have equally good and economical practical lubricating value.

Again a cylinder oil containing 25 to 30 per cent. of good fat oil might give excellent and economical results in a steam engine of 100 to 150 pounds pressure per sq. in. and where the exhaust steam is not condensed or used over again in the boiler, and be very objectionable in connection with superheated steam and where surface condensers are used. The reason, of course, is obvious.

*Thirteenth, Fourteenth, Fifteenth and Sixteenth.*—Other things being equal, the less free fatty acids present the better.

The presence of petroleum acids, sulphuric acid, sulphonates and chemicals from imperfectly refined petroleum oils should always be carefully investigated, as the presence of these foreign materials in a lubricating oil, at least for certain important services, might lead to serious trouble and complications. A first-class lubricating oil should be free from, or at least only contain traces of, these impurities.

*Seventeenth, Sulphur.*—In general very little attention is paid to the sulphur and organic sulphur compounds that may be present in a lubricating oil.



In the future the sulphur in lubricating oils will have to be reckoned with when these oils are intended for turbine service, or in services where the oil is used over and over again as in a continued oil-circulating system, where the oil, due to continuous exposure to heat, air, moisture, metal wearings, gradually becomes oxidized and polymerized, forming acid petroleum products, changing it both chemically and physically. The sulphur compounds present in the oil largely augment the corrosive or pitting action on the bearings and journals under these conditions.

In the examination of lubricating oils for sulphur content, it is important to make a distinction of how the same occurs in the oil. I have often found that in making sulphur tests by burning a given amount of oil in lamps and taking up the products of combustion in carbonate of soda solution, it is necessary to consume all the oil in the test lamps, and to make a determination of the sulphur compounds left in the wick; in some poorly chemically refined lubricating oils, the sulphur compounds found in the wick oftentimes amount to from 20 to 40 per cent. of the sulphur present.

*Eighteenth, Maumené Test.*—The sulphuric acid thermal test is of value in connection with tests of compounded lubricating oils.

*Nineteenth, Iodine Test.*—Omitted. Refer to standard text-books.

*Twentieth, Evaporating Tests.*—At temperatures of 212 to 300° F., by exposing the oil in shallow flat-bottomed dishes in an air bath at 212 to 300° F. for six hours, noting the percentage of loss and condition of residue and its behavior when mixed with 88° gasoline, we obtain valuable information as to the amount of volatile matter at low temperatures.

*Twenty-First, Heat Tests.*—For certain service, such as for air compressors not water-cooled, turbines, etc., valuable data may be obtained by exposing the oils in shallow flat-bottomed dishes in a covered air bath through which air is blown for six hours at temperatures of 425 to 540° F.; and study the residue in the dish by dissolving the same in 88° gasoline, noting whether the gasoline solution is clear or turbid and the amount of precipitate, if any, on standing.

*Twenty-Second, Emulsifying Tests.*—To determine the adaptability of an oil for lubrication in turbines of the Curtis type (step-bearing) it is of the utmost importance to ascertain the behavior of the oil when coming in contact with steam through the step-bearing, whether it forms a thick, creamy emulsion or separates from the steam and condensed water.

#### FRICTIONAL TESTS.

To make frictional tests of oils and greases of practical value requires, as indicated, testing machines so constructed that various loads, speeds, size of journal and bearings, and methods of applying the

lubricant, comparable to those in actual service as well as devices to keep journal and bearing at any desired constant temperature during the tests.

The constant temperature tests are of importance not only for the purpose of standardizing the machine for each test so as to get all conditions, bearing, journal, and feed, etc., properly regulated before the actual tests begin, but equally so in making comparative frictional tests of two oils, which have practically the same viscosity.

The two oils may show practically the same friction at a given temperature, but to keep the journal and bearing at such temperature, one oil may require a great deal more water or steam to pass through the journal and bearing; again the two oils may give practically the same friction at a temperature of say 150° or at 125° F., but great difference at 90° or at 70° F.; therefore, the constant temperature frictional tests are of great value in conducting comparative tests.

As a rule the reports of frictional tests are very incomplete; the report should give all the constants and data taken during the frictional tests, such as area of contact, projected area, total pressure on journal in pounds, pressure by square inch in pounds, total, maximum, minimum and average friction in pounds, and coefficient of friction, temperature of journal and bearing number of revolutions and feet traveled by rubbing surface per minute, duration of tests, constant or freely increasing temperature, method and amount of lubricant fed besides complete chemical, analytical data.

If two oils or greases are submitted for comparative tests where the service conditions are uniform or fairly constant, such as in mills or power-houses, the comparative viscosity and congealing or fluidity points and friction, other things being equal, would establish the most economical or suitable oil or grease for the service. But in making comparative tests, chemical, physical and frictional, of lubricants where the service conditions vary much, especially as to climatic conditions, it should be borne in mind that while the two oils submitted may show considerable difference in viscosity, congealing or fluidity point and friction, one oil may be equally good for the service requirements as the other; that is, supposing a consumer requests two oil manufacturers to submit samples for comparative tests. They may submit one sample intended to do the service for the whole year, or they may submit samples for the different seasons which latter would be the proper thing, then the samples for each season could properly be submitted to comparative frictional and other tests, otherwise not.

#### GALENA OIL TESTING MACHINE.

This machine was specially constructed and built for the Galena-Signal Oil Company, by Tinius Olsen &

# SKETCHES OF DIFFERENT VISCOSIMETERS.

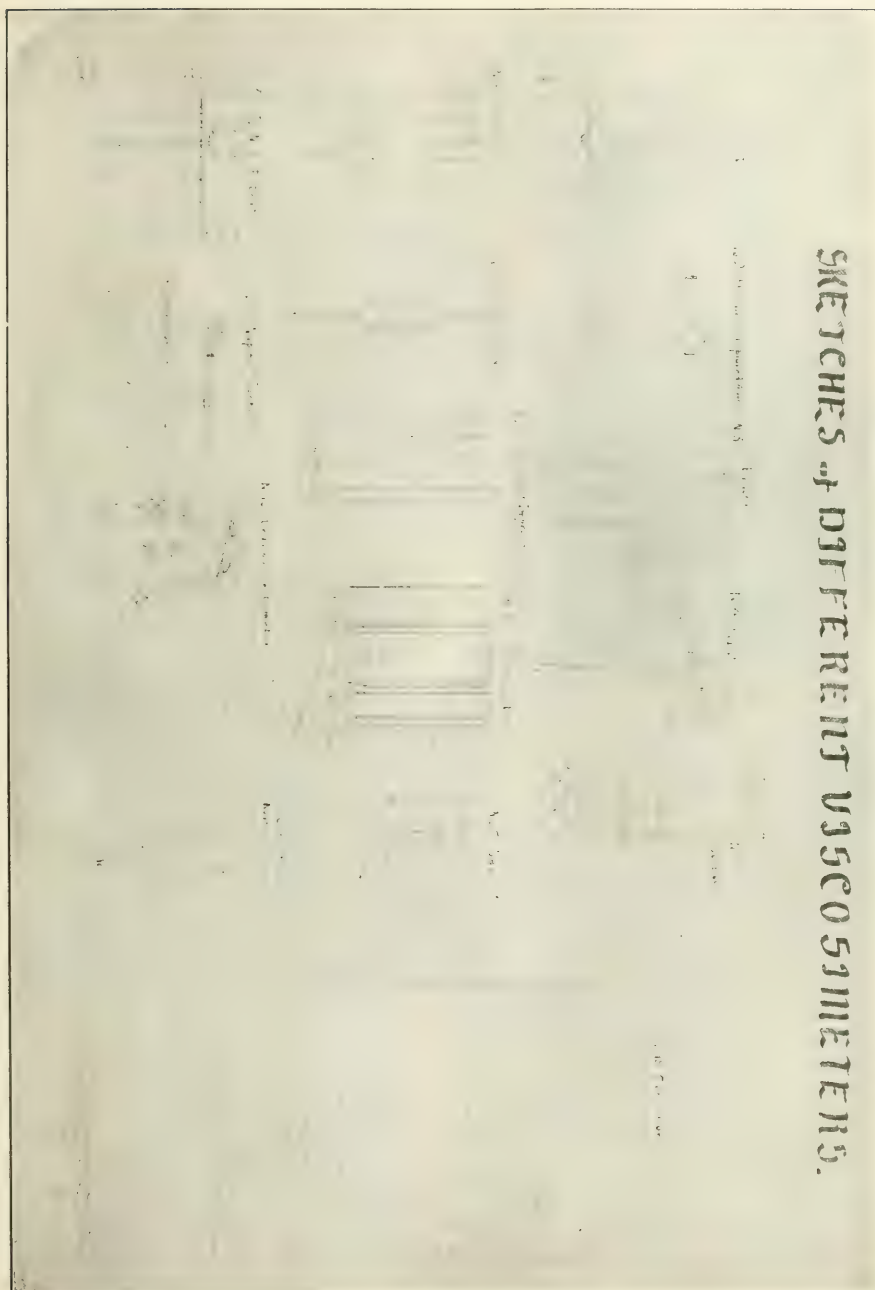


Fig. 3.

Co., Philadelphia, and is the largest and most complete ever made in this country, having a capacity up to 20,000 pounds load on the test-bearing.

It is constructed in such a way that full-size M. C. B. car journal boxes and bearings can be inserted;

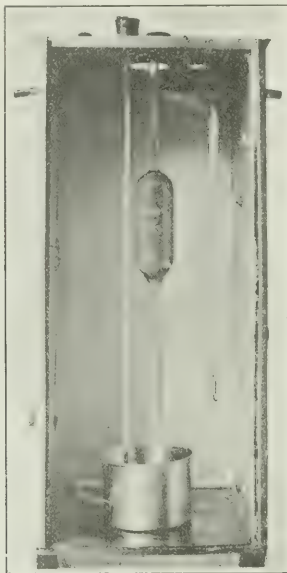


Fig 4 Dr. Chas. B. Dudley viscosity pipette

the test journals to the machine are  $4\frac{1}{4} \times 8$  in. and  $5 \times 9$  in.; by means of a leverage, screw and spring balance system, varying loads up to 20,000 pounds can be applied on the test journal while the machine is running in either direction, at any desired speed up to its maximum.

The machine is provided with a very complete and ingenious leverage and balancing system for automatic measuring and weighing of the load indicated on a dial and the friction in pounds on the periphery of the journal recorded on the scale beam in front of the machine.

It is provided with temperature indicator, revolution counter and tachometer, besides an autographic arrangement which shows the friction corresponding to the number of turns the machine makes.

The test journals and bearings are provided with a device for passing either water or steam through during the tests.

Arrangements for any desired method of applying the lubricant during the test are also provided.

The motive power is an electric motor of special construction so that the machine can be run in either direction at any desired speed, from the slowest to the fastest or *vice versa* during the test, without having to stop the same.

#### VISCOSIMETERS.

The cuts show two viscosimeters, the Redwood and Dudley pipette; the Redwood viscosimeter as shown in the cut is so well known that no further description is necessary.

The Dudley pipette as seen is a 100 cc. pipette with a mark on the stem both above and below the bulb; the viscosimeter is placed in a closed box provided with a glass door, and the temperature in the box kept during the test at the same temperature as the oil; this is of the greatest importance, taking the viscosity with an instrument of this kind.

In connection with the foregoing the following tables are of interest.

Table 1.—Nos. 1, 2, 3, 4 and 5 are the same oil fractionated by means of Florida fuller's earth. While the flash and fire test and gravity remain practically

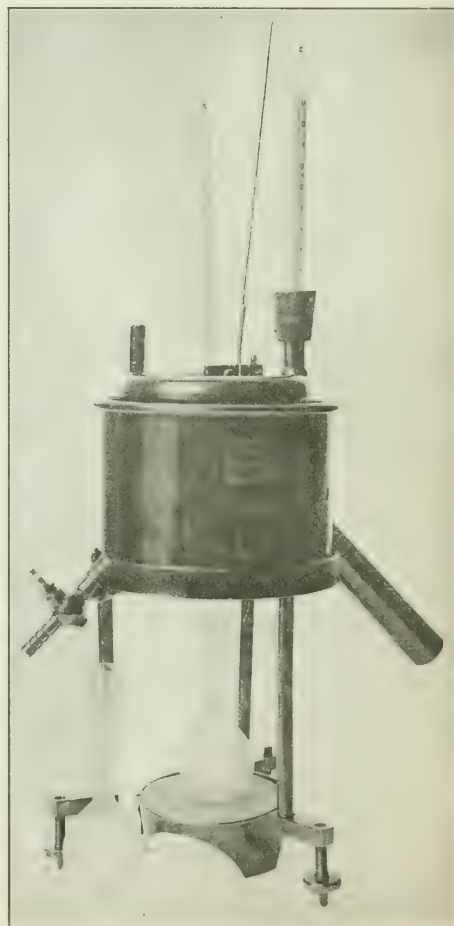


Fig 5 - Redwood viscosimeter



the same, with changes in color and some in viscosity, the congealing or fluidity point has as seen during the successive stages materially changed from the original No. 1. Nos. 6 and 7 represent an oil before and after being in continuous service in an oil-circulating system about ten months. Here again the flash, fire and gravity tests remain practically the same, but the congealing point and body or viscosity have greatly

congealing points or degrees of fluidity at different temperatures.

Table 4 gives results of frictional tests on the Carpenter frictional machine at Cornell University of a Galena railway summer oil, with increasing load on the journal from 135 pounds to 878 pounds per square inch—a sort of endurance test to determine the load capacity of the oil. From the results obtained

TABLE 1.—LUBRICATING OILS

	1	2	3	4	5	6	7
Flash point.....	365° F.	370° F.	370° F.	370° F.	370° F.	410° F.	415° F.
Burning point.....	440° F.	440° F.	440° F.	440° F.	440° F.	470° F.	480° F.
Grav. at 60° F.....	30° B.	30 7° B.	30.5° B.	30.3° B.	32.0° B.	23.0° B.	22.8° B.
Color.....	Very dark	Yellowish	Orange	Red	Deep red	Red	Dark red
Cold test.....	Zero	+18° F.	+25° F.	+25° F.	+25° F.	+5° F.	+20° F.
Viscosity (P. R. R.) pipette:							
At 125° F.....	98	92	94	94	93	85	162
" 100°.....	160	149	148	153	151	143	309
" 90°.....	205	184	192	195	195	188	410
" 80°.....	271	238	249	254	254	253	Drops

changed during continuous service. Petroleum acids and polymerized products have formed to a considerable extent; the adaptability or durability of an oil like this is seriously questioned for the service in which it is used. Have we any laboratory test (frictional, physical, or chemical) that would reveal the unsteadiness of this oil? This is a practical question that practical men want to know, and to make laboratory tests of real practical value, problems of this nature must be satisfactorily worked out and answered.

some interesting curves as to friction and temperatures could be plotted. The main point, however, is to show that the oil after the pressure on the journal gets above 400 pounds per square inch, and to the maximum load used in the test, the coefficient of friction remains practically stationary, and would give a nearly horizontal curve. From a practical standpoint this information is of great value.

Table 5.—We find first three series of tests at constant but different temperatures; second, two

TABLE 2.—GALENA CAR. COACH AND ENGINE OILS, SHOWING WIDE RANGE OF VISCOSITY AND COLD TEST.

Dudley viscosity pipette, 100 cc. water at 60° F. (15.5° C.) 32 sec.  
Redwood viscosimeter, 50 cc. rape-seed oil at 60° F. (15.5° C.) 535 sec.  
Viscosity taken at 100° F. (37.7° C.).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Time in seconds.														
Dudley.....	104	125	140	162	177	195	220	252	276	300	320	348	375	401	426
Redwood.....	151	183	204	240	260	283	335	378	392	444	480	510	556	595	650

Viscosity taken with Dr. Dudley viscosimeter, 100 cc. water at 60° F. (15.5° C.) 32 sec.  
Instrument kept in air bath at same temp. of the oils.

Time in seconds.														
125° F. (51.6° C.)	67	71	86	109	125	138	150	171	197					
100° F. (37.7° C.)	96	99	132	185	214	247	277	318	370					
90° F. (32.2° C.)	115	124	170	243	291	321	362	422	509					
80° F. (26.6° C.)	141	156	216	318	380	439	501							
	Flash point open cup.				Burning point.				Grav. at 60° F. Baumé.				Cold test.	
Summer:														
Car.....	350-380° F.				425-450° F.				26.1-27.7°				+20-+40° F.	
Engine.....	350-380° F.				425-450° F.				25.4-26.4°				+20-+40° F.	
Coach.....	350-380° F.				425-450° F.				24.3-24.6°				+20-+40° F.	
Winter:														
Car.....	210-300° F.				260-380° F.				27.4-29.0°				—5-+10° F.	
Engine.....	210-300° F.				260-380° F.				26.6-27.9°				—5-+10° F.	
Coach.....	210-300° F.				260-380° F.				25.5-26.4°				—5-+10° F.	

Table 2 gives comparison between two viscosimeters, and illustrates the wide variation in congealing points or cold tests and viscosities possessed by first-class railroad car lubricating oils; a close study of this table is of great assistance to the practical user of lubricants.

Table 3 is of great interest in connection with viscosity and cold test or fluidity of cylinder oils both compounded and straight petroleum oils, indicating the necessity of additional data in taking the

series of great difference in speed (300 and 600 r. p. m.), all other things being the same; third, comparative tests of a purely vegetable oil (rape-seed) with a compounded petroleum oil (Galena lead oxide process) with viscosities not far apart, as measured with the pipette viscosimeter; fourth, the difference in friction of the two oils at the slower speed (300 r. p. m.) is very small, while the difference at the greater speed (600 r. p. m.) is considerable, the Galena oil having a much lower friction. This is very instructive when

we consider the nature of these two oils, as well as the great load and speed.

Table 6 gives an interesting comparison between a winter and summer Galena car oil. Both have sufficient body to carry the heaviest load and speed in railroad service, but owing to the present method of conveying the oil to the car journals, a thick and sluggish oil with an unnecessary high viscosity is or has to be used during the warm or hot weather, naturally increasing the total train journal resistance, which, of course, means excessive coal consumption. Note the great difference in the fric-

Second, the necessary requisites or qualities that a first-class lubricating oil should possess in a high degree may be enumerated as follows: Necessary body to withstand the severest pressure in the service for which the oil is intended, so as to keep the rubbing surfaces apart, forming a continuous film between the same, filling up the inequalities in the surfaces; the quality of spreading itself rapidly over the rubbing surfaces, with the requisite degree of adhesive power to remain between the rubbing surfaces without creating undue friction and heating; requisite mobility or fluidity at all seasons of the year, and all climates

TABLE 3.—CYLINDER OILS.

	1.	2.	3.	4.	5.	6.	7.	8.
Flashing point.....	560° F.	595° F.	525° F.	525° F.	520° F.	515° F.	545° F.	550° F.
Burning point.....	.....	.....	600° F.	.....	.....	.....	.....	600° F.
Color.....	Very dark	Very dark	Light filter	Light filter	Light filter	Light filter	Reddish	Dark
Viscosity ( Saybolt) at 212° F.....	196	212	126	146	112	83	136	145
Cold test.....	+30° F.	+48° F.	+55° F.	+60° F.	+50° F.	+55° F.	+40° F.	+32° F.
Barely flows from thermometer at.....	+30° F.	+50° F.	55° F.	+60° F.	+50° F.	+55° F.	.....	+32° F.
Fair at.....	+40° F.	+60° F.	+60° F.	+65° F.	+60° F.	+60° F.	.....	+40° F.
Fair to good at.....	+50° F.	+70° F.	+70° F.	+70° F.	+70° F.	+70° F.	.....	+45-50° F.
Quite thick at.....	+60-65° F.	+70-80° F.	+70-75° F.	+70-80° F.	+70-80° F.	+70-80° F.	.....	+60° F.
Saponifiable fat.....	.....	.....	.....	.....	10%	33%	.....	.....

tional resistance between these oils. Practical rail-  
roaders should ponder a little more on these facts  
and utilize such knowledge.

In conclusion, what function should a lubricant  
perform? What are the necessary requisites or  
qualities that should be inherent in a first-class lubri-  
cating oil? These are trite questions, and will be  
answered briefly:

First, the function of a lubricant is to keep the  
rubbing surfaces (journal and bearing) apart to prevent  
undue abrasion, friction and heating.

from the coldest to the hottest, without impairment  
of the necessary intrinsic lubricating body for the  
required service; durability, freedom from mineral  
and organic impurities, tarry and asphaltic matter,  
unaffected by atmospheric conditions, non-drying,  
non-gunning; these are the essential qualities that  
a first-class lubricating oil should and must possess  
in a high degree.

Yet no matter how excellent and suitable a material  
or machine may be if it is not properly applied or used,  
the best and most economical results are not obtained.

TABLE 4.—FRICTIONAL TESTS OF GALENA SUMMER OIL, CARPENTER MACHINE

Bearing metal, brass; journal, steel; bearing surface; length, 3.9 in.; diameter, 3.75 in.; width, 1.9 in.; area, 7.4 in.

Number of test.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Pres. on jour., lbs. total.....	1000	2000	3000	3500	4000	5000	5500	6000	6500
Pres. on jour., lbs. per sq. in.....	135	270	405	475	540	675	743	810	878
Method of lubrication.....	Flooding bearing.								
Min. coef of friction.....	0.020	0.019	0.0163	0.016	0.0156	0.0158	0.0153	0.0152	0.0151
Max temp. of journal F.....	109	114	115	118	122	134	136	140	144
Temperature of room F.....	68	68	68	69	68	70	71	71	71
Elev. temp. jour. ab. room.....	41	46	47	49	54	64	65	69	73
Rev. of journal per min.....	215	220	220	220	223	220	220	220	185
Ft. trav. by rubbing surf per min...	211	216	216	216	219	216	216	216	182

Time	Rev. per min.	Temp. jour- nal, F	Tot. fric., lbs.	Coef. fric	Time	Rev. per min.	Temp. jour- nal, F	Total fric., lbs.	Coef. fric
1: 8.40	210	106	20	0.020	6: 10.50	220	133	79.1	0.0458
45	218	107	20	0.020	55	220	134	79.1	0.0158
50	216	109	20	0.020	11.00	220	134	79.1	0.0158
2: 9.00	220	112	38	0.019	7: 11.10	220	135	84.0	0.0153
05	222	114	38	0.019	15	219	136	84.0	0.0153
10	218	114	38	0.019	20	221	136	84.0	0.0153
3: 9.20	220	114	49	0.0163	8: 11.30	220	138	92.0	0.0153
25	220	114	49	0.0163	35	218	140	92.0	0.0153
30	220	117	49	0.0163	40	221	140	92.0	0.0153
4: 9.40	220	117	56	0.016	9: 11.50	214	142	104.0	0.0160
45	220	117	56	0.016	55	180	144	104.0	0.0160
50	220	118	56	0.016	58	160	145	104.0	0.0160
5: 10.00	216	120	63	0.0157	10: <sup>1</sup>				
05	218	121	63	0.0157					
10	234	122	63	0.0157					

<sup>1</sup> Journal stopped at 11.58; pressure 6500 lbs.

This has brought about the idea of oil manufacturers employing practical and experienced men educated in actual service to follow up and watch the proper application and economic use of the various lubricating oils and greases. These men have demonstrated, not only to their employers, but also to the consumer, the practical and economic value of their educational work.

TABLE 5.—CONSTANT TEMPERATURE TESTS, GALENA OIL TESTING MACHINE.

Comparative frictional tests between pure rape-seed oil and winter Galena railroad car oil (zero cold test oil).

Steel journal, size  $3\frac{1}{2} \times 9\frac{1}{2}$ ; bearing, genuine babbitt; total load on bearing, 10,000 lbs.; projected area, 15.5 sq. in.

Area of contact, 16.40 sq. in.  
Pressure per sq. in. projected area, 645 lbs.

Manner of lubrication, oil-bath.  
300 revolutions per min. = 392.5 ft. surface speed, average friction of four tests for each temperature.

Rape-seed oil.		Winter Galena car oil.	
Total fric. in lbs.	Coef. of friction.	Total fric. in lbs.	Coef. of friction.
56° F.....21.06	0.00211	80° F.....20.37	0.00205
70° F.....15.375	0.00154	70° F.....14.54	0.00146
90° F.....13.875	0.00139	90° F.....12.75	0.00128

600 revolutions per min. = 785 ft. surface speed, average friction of four tests for each temperature.

Rape-seed oil.		Winter Galena car oil.	
Total fric. in lbs.	Coef. of friction.	Total fric. in lbs.	Coef. of friction.
56° F.....26.25	0.00263	60° F.....19.94	0.00199
70° F.....25.375	0.00254	70° F.....18.31	0.00183
90° F.....19.75	0.00198	90° F.....15.31	0.00153

Viscosity (P. R. R.)

Rape-seed oil.	Winter Galena car oil
At 125° F.....80 units	72 units
100° F.....125 "	104 "
90° F.....141 "	125 "
80° F.....186 "	160 "
Cold test.....+15° F.	—5° F.

By constant temperature is meant that the oil-bath and bearing is kept at uniform constant temperature during the whole time of test, which lasts not less than one hour after the desired constant temperature of oil and bearing is reached.

The importance of this "following up" is far-reaching. It has gradually brought about much more systematic and uniform method or methods in lubrication, it has brought about greater economy in the consumption of lubricating oils, and at the same time demonstrated better lubrication; in fact, in many instances brought down the consumption of oil from 50 to 100 per cent., without impairment of the best and most economic lubrication. This, of course, means a saving of large sums of money by the consumers, and satisfaction to the company in the knowledge of giving its patrons the best possible service.

From these remarks, you will readily appreciate that to make laboratory tests of lubricants of real practical value, not only to the consumer but also to the manufacturer, involves considerable technical and practical knowledge and experience, besides full and complete laboratory equipment, and the chemist or engineer who is called upon to give a qualified opinion as to the relative, comparative lubricating values of two oils or greases for a given service, considered from

a practical and economical service standpoint, has indeed a difficult and oftentimes thankless task to perform.

TABLE 6.—CONSTANT-TEMPERATURE TESTS, GALENA OIL TESTING MACHINE.

Steel journal,  $5\frac{1}{2} \times 9\frac{1}{2}$ ; bronze bearing; 7800 lbs. total load on bearing; 300 lbs. pressure per sq. in.; 27.7 sq. in. area of contact; 363 rev. per min. = 475 feet surface speed; manner of lubrication, oil-bath; average friction of four tests for each temperature.

	Galena winter car oil, lbs.		Galena summer car oil, lbs.	
Temp. 65° F.				
Friction, right.....	18.50	18.50	41.00	41.00
Friction, left.....	18.50	18.50	41.50	41.50
Friction, average.....	18.50		41.25	
Coef. of fric.....	0.00237		0.00529	
Mean resistance per sq. in. of surface.....	0.665 lb.		1.489 lbs.	
Temp. 80° F.				
Friction, right.....	15.50	15.00	29.50	28.50
Friction, left.....	15.00	15.00	30.25	29.50
Friction, average.....	15.125		29.44	
Coef. of fric.....	0.00196		0.00377	
Mean resistance per sq. in. of surface.....	0.546 lb.		1.063 lbs.	
Temp. 100° F.				
Friction, right.....	11.25	11.00	20.00	20.00
Friction, left.....	10.00	10.00	20.00	20.00
Friction, average.....	10.563		20.063	
Coef. of fric.....	0.00135		0.00257	
Mean resistance per sq. in. of surface.....	0.382 lb.		0.724 lb.	

The mean resistance per square inch of surface obtained by dividing the average total friction by the number of square inches (27.7) area of contact.

	Galena winter car.	Galena summer car.
Flashing point.....	315° F.	395° F.
Burning point.....	370° F.	455° F.
Gravity at 60° F.....	27.3° Bé.	24.3° Bé.
Cold test.....	+2° F.	+36° F.
Viscosity (P. R. R.):		
Pipette, at 125° F.	83 units	189 units
100° F.	124 "	343 "
90° F.	156 "	473 "
80° F.	201 "	...

## METHODS OF ASPHALT EXAMINATION.

By ALBERT SOMMER

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The present chemical knowledge of bituminous substances is undoubtedly most limited, and their practical chemistry is confined to the most rudimentary tests, basing on "rule of thumb" methods rather than on an exact system of chemical analysis. The lack of such scientific analytical methods has always been felt more or less keenly, but never more than at present.

The commercial importance of bituminous products has been vastly increased by the application of those materials to country roads, and the following discourse deals largely with asphaltic materials applicable for that purpose.

Bitumen available to-day for this purpose originates largely from the following sources:



A. *Residuals.*

1. So-called "native" bitumen, such as deposits of Trinidad, Bermudez and similar ones.
2. Residues from crude petroleum oil. These may be divided into:
  - (a) Residue from pure asphaltic oils.
  - (b) Those from semi-asphaltic oils.
  - (c) And, also sometimes those from straight paraffine oils.

- B. *Distillates or Pyro Products* {
3. Coal gas tar.
  4. Water gas tar.

Inasmuch as all "natural" asphalts in class 1 undoubtedly represent residuum of petroleum, evaporated by natural causes, there is no strict dividing line between those products and the ones originating from asphaltic petroleum, reduced artificially in stills; and there being no essential, chemically differentiating features, any qualitative discrimination is unwarranted.

Furthermore, in order to become applicable, these natural products have to be softened by "fluxing," or the addition of oil residuum (especially in the case of softer road asphalts) which latter then more and more predominates and transfers into the compound its own characteristics.

Tar, however, and its derivatives are distillates or pyro-bitumen and naturally totally different from the previous two divisions.

The following is confined to a short description of methods either entirely new, or recently applied to asphaltic materials.

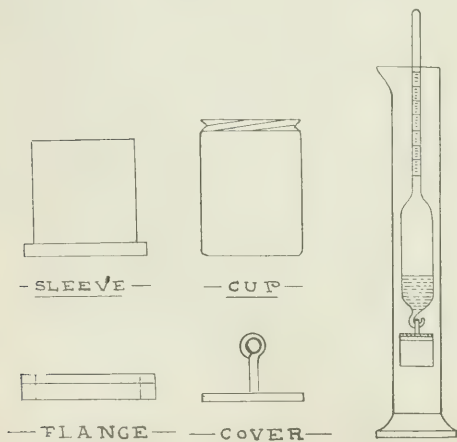
1. *Specific Gravity.*—It is remarkable how little attention has been paid to this part of bituminous research, whereas specific gravity is always one of the first means of identification of oils and other liquids.

Naturally the difficulties in determining the gravity of asphalts were considerable, inasmuch as by means of the hydrometer the gravity has to be taken at a temperature far above the ordinary one, and again, to take the gravity in a common pycnometer is also connected with the greatest difficulties on account of the shrinkage of bituminous materials when solidifying. An apparatus by which it is possible to determine the specific gravity of bitumen, in a quick and accurate way, in its normal consistency, was described by the author in a paper read before the American Society for Testing Materials, in July, this year. The principle of the method consists in letting the asphalt chill in a vessel consisting of two parts, the upper part of which takes up the shrinkage and is removed after the asphalt is chilled to a normal temperature. The lower part contains exactly 10 cc. and the gravity can be ascertained either by weighing out directly or by suspending the lower cup from a special hydrometer in water of 15.5° C.

2. *Determination of Asphalt.*—To one not familiar with commercial conditions it may appear peculiar upon first sight to hear of "percentage of asphalt" where asphalt has not as yet been chemically defined, and cannot, therefore, be determined like other chemical individuals. Nevertheless, in many instances it is essential to give a determination which is commercially satisfactory; hence a number of methods have been devised which are necessarily more or less arbitrary. The importance of determining asphaltic contents has become more appreciated since the introduction of semi-liquid asphaltic substances in the building of roads, for making so-called "bituminous macadam." It may be stated that the only reason for applying bitumen of such consistency is the necessity of incorporating it with cold stone under ordinary conditions; hard asphalt (such as is used in sheet asphalt pavement) would chill in contact with cold stone, and is therefore excluded, though it would otherwise be chosen, inasmuch as a certain hardness is required to make a satisfactory and permanent binder. For this reason such "cold" macadam binders must combine the highest percentage of hard asphalt with the highest possible fluidity, in order to be applicable; therefore the determination of asphaltic content in the same is of utmost importance to the purchaser of such materials. Unfortunately the difficulties are great and it can by no means be stated that they have at this date been solved. The present means of ascertaining the percentage of asphalt in such compounds are the following:

- (a) Precipitation with petroleum ether.
- (b) Precipitation with alcohol-ether.
- (c) In case of soft materials, evaporation until a certain consistency is reached.

It might be said that methods "a" and "b" tend to determine the percentage of asphalt by a chemical



Apparatus for determination of specific gravity.

reaction, precipitating a part of the same, while method "c" would define this percentage by reducing the bitumen to a certain, fixed, physical consistency, pronouncing anything "asphalt" which has that consistency or is harder. As to the first method with petroleum ether, it is known that petroleum ether precipitates the so-called "asphaltenes," whereas it dissolves the so-called "petrolenes." The difference between the two, however, is not sharp, as they are by no means defined chemical individuals, and their ratio is largely dependent on the solvent power of the petroleum ether used. Usually this ether is specified by gravity alone; for instance 86° Beaumé (= 0.6480 specific gravity) but it has been shown by numerous investigations by Holde, and also in the writer's laboratory, that petroleum ethers distilled from different crudes have different solvent power and that, therefore, beside the gravity, a distillation test should also be specified as lately recommended by Holde, the combination of both insuring absolute uniformity. Holde calls a petroleum ether of definite specific gravity and distillation "normal benzene."<sup>1</sup> In our laboratory we apply a distillate of 86° Beaumé gravity, distilling between 100 and 240° F. This combination of gravity and distillation tests insures a Pennsylvania product and therefore absolute uniformity in the results of precipitation. The precipitation by petroleum ether is of course not a direct measure for the real contents of asphalt, as it permits only of an approximate estimation of the same by the percentage of asphaltenes, provided that the nature of the bitumen is previously known; and furthermore, if the asphaltic material contains some light distillates, these very frequently act as a solvent and hence the precipitation with 86° naphtha shows less asphaltenes than it would if those light oils were not present. In the writer's laboratory this precipitation is performed by the following method:

Two grams of asphalt are weighed into a 100 cc. Jena glass flask, covered with 75 cc. of the normal petroleum ether mentioned above, and shaken until the entire asphalt is disintegrated. The flask is then allowed to stand over night, after which the solution is decanted and the precipitate poured into a small filter. An additional quantity of petroleum ether is then poured into the flask, rinsed and also poured through the filter, this being repeated with additional quantities of petroleum ether until the same runs off from the filter clear in color. After this a quantity of benzene is poured into the flask, which will dissolve all precipitate which may stick to the glass; then a weighted china dish is placed under the filter and the same benzene poured through the filter, the solution being received in the china dish. Benzene is applied in small quantities until all the asphalt

precipitated in the bottle, as well as on the filter, is dissolved and contained in the china dish. The benzene is then evaporated on the water bath until the dish has attained constant weight.

Should the asphalt contain anything non-soluble in CS<sub>2</sub>, this of course will have to be deducted from the asphaltenes before figuring their percentage.

*Precipitation by Ether-alcohol.*—This method is not much in use in this country, although it combines a good many advantages, as will be shown further below by experimental data. Ether-alcohol precipitates not only asphaltenes but also the softer components of asphalt, and is therefore used especially to determine the total amount of asphaltic matter in crude oils, etc. The tables below will indicate that the method can also be well adopted for the determination in fluxes and harder bitumen.

The procedure for such grades is as follows:

Two grams of the asphalt are weighed into a 100 cc. graduated cylinder with a well-fitting glass stopper, and 40 cc. of a mixture of alcohol-ether, consisting of four parts alcohol and three parts ether, poured in the same cylinder. The same should then be attached to a shaking device and shaken well for about twenty minutes. After this time it should be left to stand over night, and should be filtered in the same manner as described with petroleum ether, only the same mixture of alcohol-ether should be used until all the soluble parts are removed from the precipitate. Benzene is then used in the same manner as above described, and the weighing and calculation made in the same manner as with the asphaltenes.<sup>1</sup>

*Determination of Asphaltic Contents by Evaporation.*—

This is the one most generally used in this country, especially on softer bituminous products. A certain quantity of asphalt is evaporated in a dish of certain dimensions, at a certain temperature. The loss is taken and consistency of the residuum determined by the usual methods such as penetration, *i. e.*, the number of tenths of mm. which a needle, weighted with 100 grams, penetrates in the asphalt at 25° C. Ten mm. of "100 penetration" is usually the chosen standard, and the percentage of remainder of that consistency usually called "asphaltic contents." Unfortunately the percentage thus found is not always the real one, as will be shown in the following:

Regardless of origin, there are two classes of such binders on the market at present.

1. Semi-liquid oil residuum, which is drawn from the stills of a consistency which makes it applicable to cold stone because of its physical characteristics alone.

Natural and lake asphalts such as Trinidad and Bermudez, fluxed with oil residuum to consistency, would of course also belong to this class.

<sup>1</sup> Normal petroleum ether might be preferable to normal benzene on account of the similarity between "benzene and benzene."—Ed.

<sup>1</sup> In the case of oils which are very rich in paraffine this method sometimes precipitates part of the latter also. Therefore the precipitate of such oils should be repeatedly extracted with hot alcohol.

2. So-called "cut back" materials which are made from a hard but pliable asphalt by the addition of enough light distillate to render the compound applicable, with the view of having the liquid serve only as a thinner or vehicle, much the same in principle as thinning varnish.

TABLE 1.—PERCENTAGES OF ASPHALT BY VARIOUS METHODS.

	Compound "A" (asphalt base).	Residual flux "B" (asphalt base).	Residual flux "C" (semi- paraffine).	Residual flux "D" (semi- paraffine).
1 Gravity, specific.....	0.986	0.980	0.963	0.980
Beaumé.....	12	12.9	15.4	12.9
2 Viscosity, Engler, at 100° C., 50 cc. run.....	195 sec.	150 sec.	62 sec.	165 sec.
3 Asphalt by 86° naphtha	14.72%	4.56%	2.30%	4.2%
4 Asphalt by alcohol ether.....	35.40%	17.20%	18.10%	41.3%
5 Asphalt by evaporation: (a) Per cent. of 100 penetra- tion residue.....	88%	80%	68%	88%
(b) Time of evaporation	1½ hrs.	10 hrs.	12½ hrs.	10 hrs.
6 Engler distillation <sup>1</sup> :				
16", distilled oil, boil'g	170° C.	205° C.	295° C.	266° C.
5% off at.....	200° C.	325° C.	350° C.	350° C.
10% off at.....	260° C.	345° C.	360° C.	360° C.
16% off at.....	340° C.	361° C.	360° C.	370° C.
Gravity of distillate.....	38.3° Bé.	29.1° Bé.	33.2° Bé.	34.1° Bé.
Viscosity in pipette.....	11 sec.	21 sec.	18 sec.	17.0 sec.
7 Paraffine, Holde method	0.78%	0.29%	3.72%	3.35%
Melting point.....	138° F.	130° F.	121° F.	134° F.

From the standpoint of an oil refiner naturally the easiest way is to put out a product of class No. 1; whether, however, this is best from the standpoint of usefulness or efficiency is another question. This difference has been rather overlooked in the past and the results shown in Table 1 should serve as an illustration of the difference in various materials. Three types of fluxes were chosen for this investigation:

1. Compounded as above described (marked "A").
2. A residual flux (marked "B"), originated from an asphalt base petroleum as per Class No. 1, and
3. Residual fluxes (marked "C" and "D"), obtained from semi-paraffine base crude oils also per Class No. 1.

All semi-liquid asphalts used for these tests represent types of commercially available products,<sup>2</sup> such as used in actual work, and, all had nearly the same consistency, namely, semi-liquid. Table 1 shows percentages of asphalt of all these binders, as obtained by the various methods. The results of this table show that there are marked differences in true asphaltic content, which are to an extent illustrated by the results of precipitation with petroleum ether and also with alcohol-ether. The results of evaporation also show differences, but the mere percentages thus obtained do not illustrate the true nature of the various fluxes and, what is more important, do not show whether the asphalt which was thus found was already present in the flux or had been formed during the evaporation test itself. It cannot be emphasized too strongly that in all evaporation tests this will

have to be reckoned with, although very few specifications at the present time take this into consideration. One glance at the table shows that the time required for the various evaporations indicates vast differences, and this already proves that percentages of asphalt obtained by the evaporation method in an unlimited time and high temperatures are often "pseudo percentages" which are of no practical value, inasmuch as such distilling or baking will never take place when those materials are in actual use. Practical experience has in the meantime confirmed these differences.

Precipitation and evaporation combined show that the hard asphalt obtained from residual fluxes was not originally present in the same, but has been produced by distilling or "cooking" heavy oils. In other words, their consistency is due to the presence of some asphaltogenous substances, which, while not being asphalts themselves, represent, as may be said, asphalt in an embryonic state which will form asphalt by the influence of great heat and oxygen; and combined with heavy, viscous, residual oils which can only be driven off at high temperatures; whereas the fluidity of "A" is caused by the admixing of a liquid vehicle to an already present base of hard asphalt, very much like the process of making varnish out of gum and turpentine.

The writer applies a method of distinguishing those products successfully by the determination of the consistency of the distillate obtained from such compounds. The distillation is performed in an ordinary Engler apparatus. We distil off a certain percentage of the compound, noting the temperature and if the same suddenly rises or jumps this in most cases indicates presence of a light thinner, whereas a residual oil will distil off more evenly; at any rate, to distil off about 20 per cent. will be sufficient in most cases. Distillates are then compared by gravity and viscosity and results shown in Table 2 exhibit the differences which may thus be obtained.

TABLE 2.—VARIOUS RESULTS OF EVAPORATIONS UNDER DIFFERENT CONDITIONS.

	Compound "A" (asphalt base).	Residual flux "B" (asphalt base).	Residual flux "C" (semi- paraffine).	Residual flux "D" (semi- paraffine).
Evaporations on 100 grams at 500° Fahrenheit:				
(a) Open, without stir- ring; loss.....	16%	20%	33%	12%
Penetration of residue	82	95	98	92
Time.....	1½ hrs.	10 hrs.	12½ hrs.	10 hrs.
(b) Open, with stirring, loss.....	16%	20%	33%	12%
Penetration of residue	86	120	96	114
Time.....	1½ hrs.	5 hrs.	5½ hrs.	8½ hrs.
(c) In oven, without stirring; loss.....	16%	20%	30.5%	12%
Penetration of residue	73	49	97	300
Time.....	5 hrs.	19 hrs.	17 hrs.	3 hrs.

<sup>1</sup> Note: Evaporation taken on 100 grams, in 5" × 2 3/8" box, at 500° F., in the open without stirring.

<sup>2</sup> And all marketed as "90 per cent. binder."

In the second table there are exhibited results of



evaporations on the same materials as in Table 1, but under various conditions. All the evaporations in Table 1 were made on 100 grams of asphalt in a container 5 inches in diameter by  $2\frac{3}{8}$  inches deep. That there are very marked differences, regardless of the quantity and other data, and depending only on the difference in the various methods of heating is shown in Table 2, from which it can readily be seen that the oils of various bases behave very differently under varying conditions.

Therefore, it is necessary when specifying asphaltic contents, to always state the following:

1. Quantity of asphalt applied (the evaporation being a surface function, is of course largely dependent on the ratio of the surface to the volume, and will vary with varying quantities).

2. Size of vessel.

3. Temperature, and *length of time* to be exposed to the same; the latter item is evidently the most important one.

4. Whether the evaporation takes place.

(a) In a closed oven.

(b) In the open.

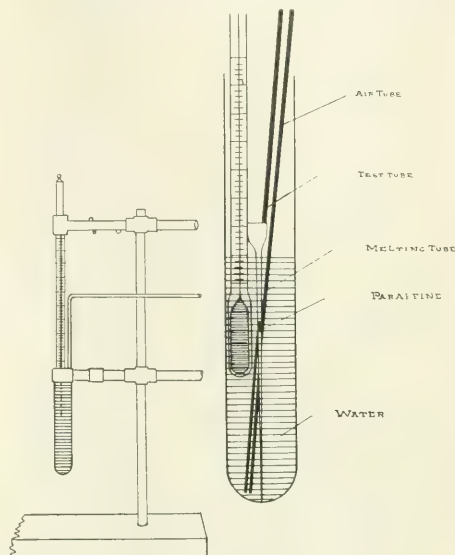
(c) With or without stirring.

2. *Paraffine*.—Next in importance to asphalt is paraffine as a distinguishing feature of petroleum. Without entering here into the question of merit or disadvantages of paraffine in asphalt, there has been a great deal of uncertainty regarding its determination. It should be remembered that paraffine is not a chemical individual, and that the percentage of crystallizing paraffine scale in a given distillate depends entirely on the solvent and also on the temperature at which this crystallizing takes place. It should also be remembered that paraffine is never contained in a crude oil or in a residual in its scaly modification, but always as amorphous, so-called "proto" paraffine. Therefore the first demand is to make the asphaltic material subject to destructive distillation to coke, and determine the scale in the distillate. In some asphalts there is no paraffine whatsoever and for this reason a qualitative test should be made first, as follows: The asphalt is distilled to coke, and a drop of the distillate is caught at intervals and put on ice. The temperature and percentage of distillate should be noted at the point when this drop chills.

Some asphalts furnish a distillate which chills at once, whereas others are practically free from paraffine scale; therefore a quantitative determination does not have to be made. The quantitative methods now in use are either the one by Zalociecki or that by Holde. Zalociecki dissolves the distillate in amyl alcohol and precipitates with ethyl alcohol at  $0^{\circ}$  to  $-5^{\circ}$  F., whereas Holde precipitates with alcohol ether at  $-20^{\circ}$  C.

Table 3 contains paraffine determinations of various asphalts and it will be seen at first sight that

the results, although taken on one and the same material, differ vastly. This is for the reason that, as above stated, paraffine is not paraffine in every case, and that the amount of paraffine scale crystallizing out is entirely dependent on its consistency. The colder the "wax distillate," the softer is the crystallizing scale; this is in accordance with the commercial process of bringing out paraffine wax, which is marketed and designated from different "pressings" by melting point. The writer has therefore made it a practice



Apparatus for determining melting point of paraffine

to invariably determine the melting point of paraffine, and it cannot be demanded urgently enough that in all such present specifications which set a limit to paraffine scale, its melting point should also be given, as otherwise there would be no end of discrepancy. There seems to be a certain ratio between melting point and percentage, and in most cases a difference of  $2^{\circ}$  F., melting point, seems to be equivalent to one per cent. scale.

TABLE 3.—RELATION BETWEEN CONSISTENCY AND PERCENTAGE OF PARAFFINE.

Determinations	1. Zal	2. Zal.	3. Holde.	4. Holde.
No. 1 (65% binder; residual).....	16.5	15.8	4.5	.....
Melting point.....	96° F.	104° F.	120° F.	Flows
No. 2 (90% binder; residual).....	10.0	9.0	5.0	.....
Melting point.....	108° F.	110° F.	118° F.	Flows
No. 3 (95% binder; residual).....	6.2	4.3	2.7	.....
Melting point.....	116° F.	122° F.	131° F.	Semi-fluid
Compound No. 3.....	13.4	7.5	7.3	10.0
Melting point.....	105° F.	124° F.	126° F.	118° F. Liquid

For the melting point we use the capillary method. The results as exhibited in Table 2 speak for

themselves. It should be remembered in this connection that even the originators of the methods of determination do not claim accuracy within one per cent., whereas there are a number of asphalt specifications stipulating percentages within one quarter of one per cent. and even less of paraffine; this is totally objectionable especially when no melting point is given.

There are also a number of specifications having a so-called "cold test," as follows:

"When a six inch test tube, having an inside diameter of one inch is filled one half full of the oil, cooled to and maintained at 50° F., for a period of thirty minutes, then brought to and maintained at 65° F., for a period of thirty minutes, it must at that temperature (65° F.) show a flow perceptible to the eye in thirty seconds. The oil after cooling to 50° F. must not be stirred or agitated in any way before or during the flow test and after being cooled at 50° F. it must not be heated to a temperature exceeding 65° F., until after its flow has been determined."

Upon inquiring of the originators of this specification it was learned that this extremely complicated clause had the object of eliminating paraffine oils. It was stated that if such materials were to contain paraffine to any extent, they would chill at 65° F., thus not complying with the above specification. This sounds plausible enough but since we found that bitumens such as represented on Table 3, although all containing more than three per cent. paraffine, would show a flow according to this specification at 65° F., we have concluded to investigate this matter more thoroughly. A heavy Texas distillate, which contained neither paraffine nor asphalt, was taken as a neutral base. At first we dissolved in it 8 per cent. of paraffine scale of a melting point of 125° F. This compound represented a solid mass at room temperatures. We then added 8 per cent. of a soft Texas asphalt, and the result was compound No. 3, which is a thorough liquid, and more liquid even than the asphalt dissolved in the oil alone. We have, therefore, the case of a lowering of the melting point produced by the combined action of paraffine plus asphalt. Therefore, the only reason that binders 1, 2 and 3 (Table 3) are liquid at 65° F. as specified, can be sought for in the fact that they contain asphalt and paraffine. If one or the other were removed, the remainder would become harder. This we have also shown on a residual cylinder oil, of semi-asphaltic basis which contained some asphaltic matter; alcohol ether precipitated 18.5 per cent. The oil was thoroughly liquid (cold test = 75° F.). It was filtered through porous matter, which retained the asphaltic substance, and the result was a light colored product which is solid at ordinary temperatures, its cold test being 90° F. Attached is an analysis of the oil before and after filtering.

This case illustrates conclusively that the consistency of an asphaltic compound alone can never give an idea of its true contents, and that a specification like the above is utterly worthless.

3. *Determination of Tar.*—It has so far been impossible to ascertain the presence of tar except by more than very doubtful methods. The method which is herewith introduced will give, if not extremely accurate ones, results of satisfactory commercial value. The principle of the method consists in distilling the bitumen to coke, and applying dimethylsulfate to the same. Dimethylsulfate dissolves oil products of benzene character or pyro distillates, whereas it does not dissolve paraffine or olefine hydrocarbons, such as produced by the distillation of mineral oil. E. Graefe has applied this reaction to separate brown coal or shale distillate from coal tar products, and the writer found that it represents an ideal means of separating all distillates obtained from pyro-bitumen, or all benzene derivatives from petroleum distillates, which, of course, consist largely of paraffine chains or other saturated hydrocarbons.

TABLE 4.—PERCENTAGE COAL TAR BY SOLUBILITY OF THE DISTILLATE IN DIMETHYLSULFATE.

Description of product.	Solubility in per cent
E Grade petrol asphalt.....	Not soluble
Bermudez asphalt.....	" "
Cuban asphalt.....	" "
Gilsonite.....	" "
Coal tar.....	100 "
20% tar + 80% asphalt.....	15 "
40% " + 60% ".....	30 "
50% " + 50% ".....	35 "
60% " + 40% ".....	40 "
80% " + 20% ".....	60 "

Table 4 containing results obtained by this method gives the solubilities in dimethylsulfate of straight coal tar distillate, straight asphalt distillate (both native and oil), and various mixtures. The results illustrate that there is a certain fixed proportion by which we can very well judge the relative proportion of each. It is also interesting to note that all native asphalts, including gilsonite, act exactly like oil asphalts with the dimethylsulfate, which is a further proof of the identity of their origin. The importance of this method is considerable, inasmuch as the market value of tar is of course far below that of asphalt, and the lack of a method of determination has been felt very keenly. The method as executed in the writer's laboratory is as follows:

Four cc. of the distillate obtained by destructive distillation of the asphalt (to coke) are put in a ten cc. graduated cylinder with ground glass stopper, and six cc. of dimethylsulfate are added and shaken thoroughly for one minute. If the distillate is not entirely soluble, separation takes place within a few minutes and a separating mark can be accurately read. The percentage of solubility is calculated from this reading.

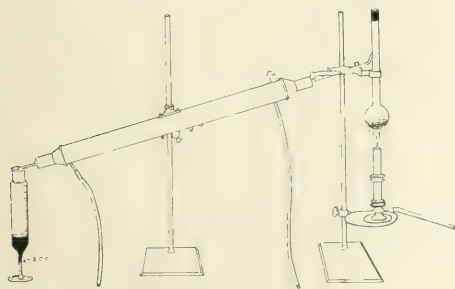
The methods outlined above may well be char-

acterized as an attempt to characterize and eventually analyze bitumina by their destructive distillate, which principle is new and I believe highly promising.

#### APPENDIX.

In the following we briefly describe a method of determination of water and one for the determination of sulphur. Both of these methods were originated by Edmund Graefe for crude oils and coal; the following describes their modification for asphaltic substances, for which they supply long-felt wants.

(a) *Water Determination.*—In distilling off water from heavy bodies such as bituminous matters or crude oil, foaming takes place which renders distillation entirely impossible. Graefe applies a light volatile oil, such as petroleum distillate or coal tar distillate, to the substance and distils both. In order to determine water in asphalt, 50 cc. of asphalt are mixed with 50 cc. of a petroleum distillate of volatile character. A product of this kind can be purchased in any quantities, it being a well-known turpentine substitute.<sup>1</sup> The total is then distilled and distillation proceeds easily and without any explosions. The same volume of the applied solvent is distilled off and thus made sure that all the water will be driven over, which, of course, settles after condensing. The combined distillates are caught in a flask having a

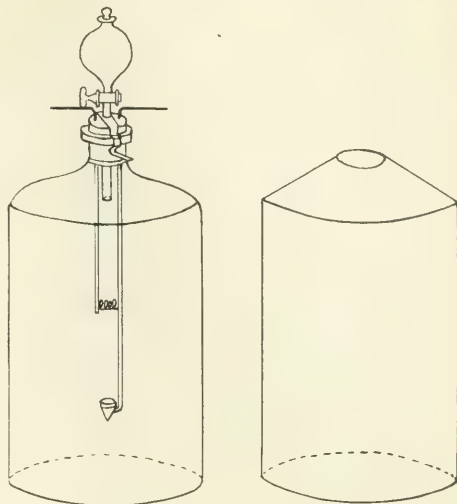


Apparatus for determination of water.

stem divided into 2 cc. This corresponds to one per cent. if 50 cc. of asphalt were applied, the water settling easily from the light distillate, and its percentage can be read at once, without any figuring.

(b) *Sulphur Determination.*—The principle of this method consists in the combustion of the bitumen in an atmosphere of oxygen. This was at first suggested by Hempel, and later modified by Graefe for coal products and was successfully applied in the author's laboratory on oils and asphalts. About 0.2 gram of bitumen are weighed and placed on a small lump of chemically pure cotton, which must be free from sulphur. This is then placed on a small platinum cone which, again, is suspended from a copper wire. The cotton containing the bitumen is connected to

a thin platinum wire, forming a short-circuit between the suspending copper wire and another wire through which an electric current can be sent coming from



Apparatus for determination of sulphur.

a dry battery. The current will thus ignite the thread, the cotton and finally the asphalt, which will burn freely in the oxygen. After combustion is completed a solution of sodium peroxide is permitted to enter the flask. Care should be taken that this be done either after the bottle is cold, or that the surplus pressure is released gradually through the solution of sodium peroxide in which case it would retain all sulphurous gases. Determination of sulphur is finally accomplished by neutralization and precipitation of the solution with barium chloride. With a sufficient number of apparatus it is easy to execute two dozen sulphur analyses per day. They are accurate almost to the theoretical point which has been established by a number of experiments.

### THE DETERMINATION OF COPPER IN BLISTER AND REFINING COPPER.

BY WILLIAM C. FERGUSON.<sup>1</sup>

Received March 18, 1910

Through the efforts of representatives of those interested in the commerce of copper, continual advances have been made in sampling and analysis with the object of securing its correct valuation.

Although the electrolytic method for the determination of copper is universally employed, marked differences exist in the detail of its performance.

A description of the method developed in the laboratory of the Nichols Copper Co. is, therefore, pre-

<sup>1</sup> The commercial name of this product is *Texene*. Its gravity is 42° Beaumé and its limits of evaporation are between 270° and 450° F.

<sup>1</sup> Chief Chemist, Nichols Copper Co.



sented with the object of interesting chemists in a movement towards uniformity of practice.

The importance of this subject will be realized when it is stated that upwards of 1,400,000,000 pounds of copper are refined annually in the United States, valued at approximately \$200,000,000 for which settlements are made upon the basis of sampling and analysis.

The method of sampling employed, vitally important in itself, will be briefly described, leading up as it does to the method of analysis.

Before describing the methods in detail, attention is directed to the following brief description of the separate steps involved. The methods are largely automatic, the limits of accuracy proved and the judgment of the manipulator reduced to a minimum.

The pieces of copper composing the parcel are drilled according to the method of squares whereby all parts are given their proportionate value in the sample.

The drillings are accurately quartered and ground very fine (20 mesh).

Six sample packages are prepared from these fine drillings. Experiment has shown that there is no material difference in the packages.

Eighty grams, an unusually large amount, are weighed out for analysis (almost one-quarter of the sample package).

The ground drillings are dissolved in a 2000 cc. flask accurately calibrated to the overflow pipette which is employed for dividing the solution for electrolysis.

The flask and pipette are surrounded by water to eliminate the influence of temperature upon the volume of the solution.

Two grams of copper are deposited on a foil much smaller than those used in laboratories with which the writer is familiar, where one gram is deposited.

A constant current is employed.

Strength of current and composition of electrolyte used have been demonstrated to give the purest deposit.

The minute quantity of impurities deposited with the copper are systematically determined and corrections applied to daily analyses.

Twice a week refined copper of known composition is put right through with the blister samples, being treated in the same way in every particular.

All of the statistical tables, illustrating the accuracy of the different steps in the method, have been compiled from consecutive results, involving *no selection* whatever, *i. e.*, all the results obtained are incorporated in the tables.

#### PREPARATION OF THE SAMPLE UP TO THE POINT OF DELIVERY AT THE LABORATORY.

Blister copper, in lots averaging forty to fifty tons, is delivered at the refinery in the form of pigs, cakes or slabs weighing from fifty to three hundred pounds each.

The method of sampling depends upon the factors

of size, value, shape, uniformity of grade and the number of pieces in the lot. But, the fundamental principles involved are the same in all cases and depend upon the fact that the average composition of individual pieces in a single lot may vary and, also, that different portions of the same piece differ, sometimes largely.

Briefly, the procedure is to drill a one-half inch hole of certain depth and position in each piece or in a percentage of the total number. The position of the hole is changed in successive pieces in such a manner that, if all the holes were drilled in a single piece, the face of which is divided into equal squares, a hole would be made in the centre of each square. The number of the squares corresponds to the number of the pieces in the lot or a ratio thereof.

By means of a funnel-shaped collar laid on the piece and around the drill, chips, other than those cut by it, are prevented from entering the sample.

Upon withdrawal of the drill the borings are brushed from the collar through the hole in the piece and a corresponding one in the table of the drill press into a receptacle underneath.

The borings from each lot, weighing from 18 to 27 pounds, are collected and ground in a sample grinder, to pass an 8-mesh sieve and then reduced to four and a half pounds by use of a trough sampler. This amount is then passed through a drug mill having chrome steel grinding plates, until ground to 20-mesh size.

Although the grinding plates of the mill show a certain amount of wear in the course of a year, investigation has shown that the particles worn from

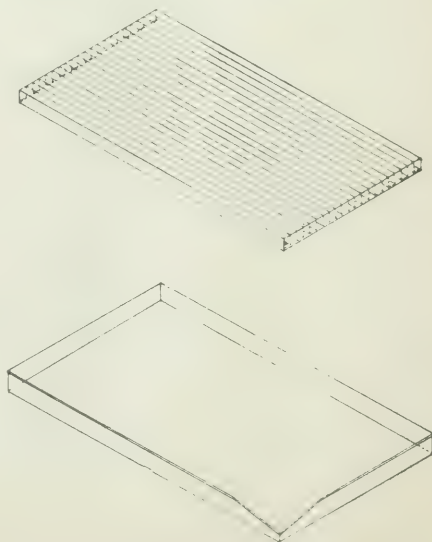


Fig. 1

the mill are quite insufficient to affect the value of the sample.

After thus grinding the quartered portion to 20-mesh size, it is then thoroughly mixed and divided by the use of a trough sampler, into six parts averaging 320 grams each.

Since the coarse and fine portions of the sample have quite different copper, silver and gold values it is essential that their relative proportions should be maintained in the division of the sample. The trough sampler (see Fig. 1.) has been found, by repeated experiments, to be more accurate than "heap quartering" in this respect.

Experiments have shown that the six portions, into which the ground drillings are divided, contain practically the same amount of coarse and fine material.

Comparison of copper results from different packages of the same sample.

Brand.	Lot.	Package. No. 1.	Package. No. 2.
A.....	106	99.26	99.26
B.....	678	99.12	99.11
	683	98.98	98.90
	703	98.84	98.78
	734	98.93	98.93
	760	99.05	99.06
	805	99.11	99.06
C.....	198	99.34	99.33
	200	99.29	99.27
	202	99.23	99.22
D.....	396	98.74	98.70
	406	98.98	99.00
	424	99.06	99.07
	428	99.04	99.03
E.....	552	98.96	99.01
	555	99.08	99.10
	562	98.82	98.84
	577	98.97	98.97
F.....	293	99.38	99.39
G.....	190	98.96	98.93
Average.....		99.057	99.048

SIEVING TESTS TO SHOW WHAT DIFFERENCE IN PROPORTION OF COARSE AND FINE MAY EXIST IN PACKAGES OF THE SAME SAMPLE

Sample. No.	Per cent. of 40-mesh fines in							
	1.	2.	3.	4.	5.	6.	7.	8.
A.....	18.27	18.19	18.11	18.23	18.34	18.19	18.15	18.09
B.....	15.61	15.26	15.47	15.58	15.34	15.34	15.50	15.56
C.....	16.93	16.62	16.76	16.96	16.78	16.77	16.98	16.91
D.....	17.43	17.82	17.64	17.61	17.90	17.56	17.38	17.49
E.....	703	18.12	18.36	.....	.....	.....	.....	.....
F.....	704	18.64	18.51	.....	.....	.....	.....	.....
	705	17.98	18.26	.....	.....	.....	.....	.....
	313	22.14	21.79	.....	.....	.....	.....	.....
G.....	312	15.93	16.07	.....	.....	.....	.....	.....
	313	16.47	16.51	.....	.....	.....	.....	.....
	314	16.11	16.48	.....	.....	.....	.....	.....
H.....	17	19.41	19.32	.....	.....	.....	.....	.....
I.....	526	21.36	21.76	.....	.....	.....	.....	.....
	527	20.86	21.07	.....	.....	.....	.....	.....

Maximum difference is 0.40% which would affect the copper results 0.016% if a difference of 4% copper be assumed to exist between the assay of coarse and fine.

MANIPULATION OF THE SAMPLE FROM THE PACKAGE TO THE FLASK.

A trough sampler is used both in the sample room and in the laboratory. The one in the sample room has troughs and spaces half an inch wide and is used for dividing the whole sample of ground drillings

into six parts as described above. The other (Fig. 2), in the laboratory, has troughs and spaces quarter of an inch wide and is used to obtain the portion for analysis from one of the six sample packages.

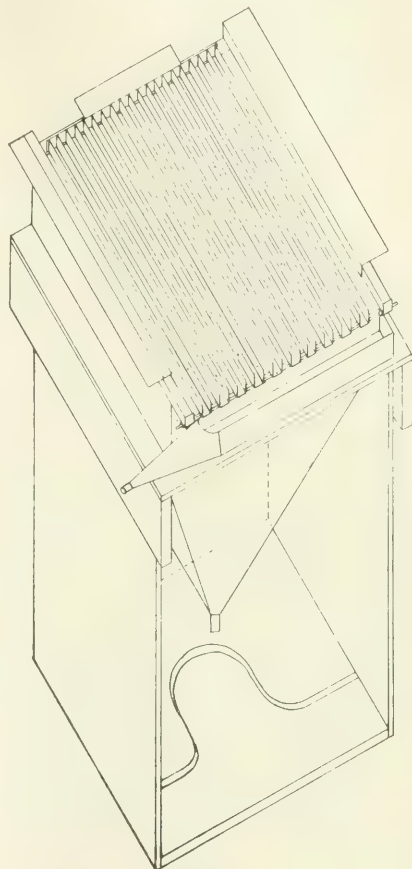


Fig. 2

In the use of both, the sample should be scattered with a motion that will allow the particles to fall in an even stream upon the troughs. A full arm, side to side, movement of the bag or pan accomplishes a very accurate division. A rotary or axial motion should be avoided.

The amount for analysis used in this laboratory is 80 grams, approximately one-quarter of the contents of the sample bag. It is an easy matter to divide the sample to within a few grams of the mathematical quarter.

Experiments by sieving have shown that the maximum difference in composition between the 80-gram portion and the remainder of the package is no more

than 0.025 per cent. in copper and that the average difference is inappreciable.

TABLE COMPARING THE TEST PORTION WITH THE REMAINDER OF THE SAMPLE BAG.

The sample packages were quartered by trough sampler to approximate 80 grams and this test portion sieved. The remainder of the contents of the sample package was then sieved in the same manner as the test portion in turn.

The quartering of the samples was done in turn by each of the several chemists employed in the determination of copper.

The copper contents of the coarse and fine portion of the samples averaged 5% apart and this figure is used in calculating the difference in assay value between the test portion and the remainder of the sample.

Brand.	Lot.	Per cent. of test portion.	60-mesh fine remainder of sample.	Fine in test portion.		The difference of per cent. of fine between the test portion and the remainder makes the copper content of the test portion.	
				Higher.	Lower.	Higher by.	Lower by.
A.....	74	13.38	13.77		0.39		0.020
	77	12.10	12.61		0.51		0.025
B.....	449	11.32	11.23	0.09		0.005	
C.....	51	14.53	14.86		0.33		0.016
D.....	444	12.59	12.12	0.47		0.024	
E.....	120	11.83	12.15	0.32		0.016	
F.....	818	11.51	11.41	0.10		0.005	
G.....	588	13.92	13.52	0.40		0.020	
H.....	678	9.40	9.58		0.18		0.009
	679a	12.91	12.74	0.17		0.009	
	679b	12.51	12.54		0.03		0.002
Average.....				0.26	0.29	0.013	0.015

The borings resulting from the division are placed in a clean test tube and thoroughly shaken before taking to the balance. The entire contents are discharged into the balance pan, the tube being held in a perpendicular position and slowly withdrawn while being revolved on its axis.

If the amount on the balance pan is found to be over 80 grams, portions are taken off by the spatula midway between the top and the bottom of the heap. If less, the sample in the bag is thoroughly shaken and the deficiency made up by taking the required amount with a spatula from the bag.

After weighing exactly 80 grams, the ground drillings are brushed from the balance pan into a chute which is then inserted in the neck of a tilted 2000 cc. flask.

The chute (Fig. 3) is made by folding a smooth piece of writing paper, nine inches long and  $3\frac{1}{4}$  inches wide, once over on the double fold and then unfolding. This chute completely envelops the ground drillings during insertion and prevents loss of fines.



Fig. 3

By bringing the flask to an upright position, the drillings will fall to the bottom without allowing fine particles to adhere to the neck. The chute is brushed downwards while being withdrawn from the flask.

The "coarse and fine" as well as the "catch

weight" methods have been compared, on numerous samples, with the practice of weighing out exactly 80 grams. As will be observed from Tables D and E, the results by the several methods average practically the same in the long run.

#### D.

The "coarse and fine" method consists of sieving the entire contents of the sample package through a 40-mesh screen. The siftings and portion left on the screen are each weighed in order to ascertain their percentage to the entire sample. The coarse is then quartered by use of the trough sampler to about 80 grams. Exactly 80 grams are weighed out and assayed according to the regular procedure. The whole of the fine, which varies from 40 to 90 grams, is taken for assay according to the regular procedure. From the data thus obtained the per cent. copper in the sample is calculated.

This method eliminates completely the question of proportion of coarse and fine in the test portion.

Brand.	Lot.	Regular 80-gram method.	"Coarse and fine" method.
A.....	1	99.46	99.42
B.....	47	98.47	98.44
C.....	46	98.33	98.38
D.....	61	98.98	98.91
E.....	61	98.81	98.86
F.....	187	98.88	98.91
G.....	748	98.55	98.59
H.....	21	99.09	99.12
	36	99.05	98.96
	40	99.02	99.01
	41	98.96	98.97
	43	99.15	99.13
	854	99.29	99.26
	855	99.26	99.31
I.....	184	99.84	99.12
	218	99.14	99.15
	269	99.08	99.05
J.....	131	99.29	99.21
	135	99.43	99.35
	138	99.40	99.47
	147	99.36	99.38
	544	99.28	99.21
K.....	166	99.22	99.22
	168	99.20	99.16
	171	99.21	99.17
	444	99.05	98.99
Average.....		99.073	99.067

#### E.

COMPARISON OF DIFFERENT METHODS OF WEIGHING-OUT PORTIONS FOR ANALYSIS.

The method of "catch" or "struck" weights consists of quartering the contents of the sample package by the trough sampler, but, instead of weighing out exactly 80 grams, the whole product of the quartering which may vary several grams more or less than the required amount, is used for analysis.

The following table shows how results by the two methods compare:

Brand.	Lot.	"Catch weight" approximately	
		80 grams weighed out.	80 grams weighed out.
A.....	127	99.04	99.02
B.....	138	99.04	99.04
	140	99.01	99.00
	150	98.92	98.92
C.....	313	99.28	99.31
	315	99.37	99.35
D.....	91	99.30	99.26
	106	99.28	99.27
	113	99.30	99.30
E.....	493	99.32	99.34
	497	99.27	99.20
	500	99.15	99.16
F.....	428	99.04	98.97
	449	98.98	99.05
	543	98.82	98.80
	552	98.94	98.97
G.....	32	97.64	97.65
H.....	250	99.25	99.29
I.....	28	98.52	98.50
J.....	92	99.37	99.36
Average.....		99.042	99.038



## CALIBRATION OF THE FLASKS.

Calibration of the flasks, to the automatic dividing pipette, by the method of repeated delivery, is done by two men working independently and employing for the purpose the regular type of solution used in daily copper determinations.

A difference of one-tenth cc., the equivalent of 0.005 per cent. copper, is easily discernible on the narrow necks of the 2000-cc. flasks and the analysts check each other within that limit.

It has been determined that, throughout the range of normal room temperature, a difference of  $1^{\circ}$  F. causes a change of volume of 0.46 cc. in 2000, and, since this amount will affect the copper result to the extent of 0.023 per cent., extreme precaution is taken to keep the temperature of the solution constant during the process of calibration.

The flask, during the operation of standardizing, is placed in a small tank through which water, of the same temperature, is flowing from a larger tank. The water in the larger tank surrounds the reservoir of copper solution which is to be siphoned to the pipette (Fig. 4).

Immediately after the requisite number of the deliveries have been made, the flask is placed on a fixed level table while the volume mark is scratched on the neck with a diamond pencil.

The system of water-jacketing obviates entirely all temperature corrections, the maximum variation in temperature of the solution during standardizing being  $0.2^{\circ}$  F.

The temperature observations are made with long-stemmed thermometers graduated into tenth degrees F.

It has been demonstrated that, in the solution of the ordinary brands of blister and refined copper, the viscosity is the same, and therefore, the rate of flow from the pipette is not affected.

During the process of calibration the evaporation of the copper solution running into the flask has been found to be insufficient to cause appreciable error.

*Dividing Pipette.*—The 50 cc. dividing pipette (Fig. 4) has a capillary overflow and three-way stop-cock and is water-jacketed

for a purpose which will later be explained. This pipette, when constructed in the proper manner, delivers with great accuracy and speed.

The stop-cock and delivery bore should be along the axis of the body of the pipette. For ease in handling, the stop-cock should be rather large.

The delivery bore should be so constructed as to give an unbroken stream for four inches, and there should be no tendency for the retained liquor in the delivery end to spread and draw up on the outside of the tube, nor to run out after delivery for at least a minute.

The manipulation of the stop-cock should always be uniform in manner and speed, the knack of which is readily acquired.

The supply tube, which is also water-jacketed, is connected with a removable siphon which dips

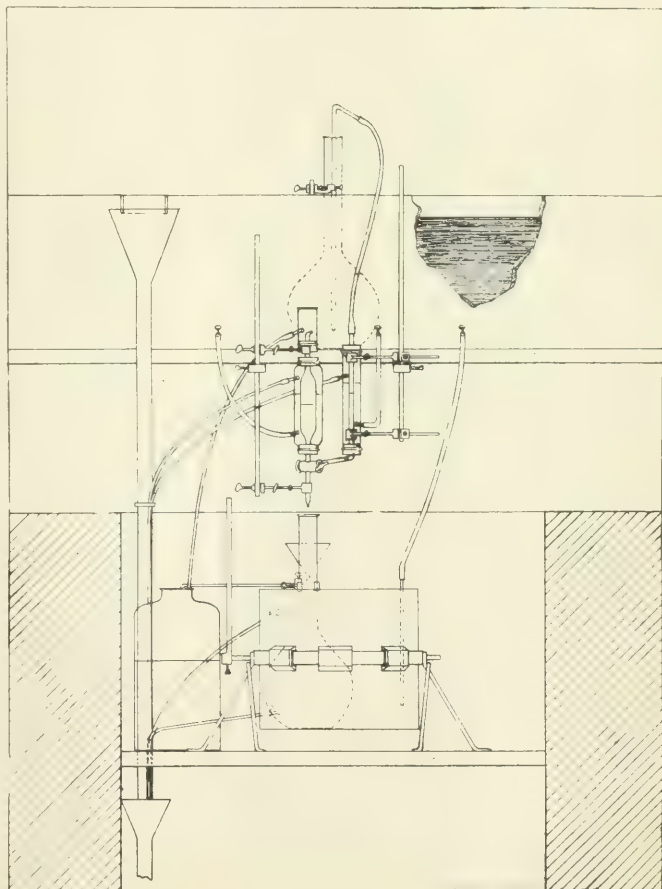


Fig. 4.

into the body of the flask containing the copper solution. On the end of the siphon is a filter of fine bolting-cloth. Suction applied to the pipette starts the action of the siphon.

The delivery of the pipette and the skill of the operator are tested weekly by running off four deliveries from the pipette into 50-cc. glass-stoppered tared flasks.

From our record of the weight of deliveries during the last nine months, the largest average variation in a trial set of four draughts is equivalent to 0.014 per cent. of copper while the average variation in all the trials during this period is equivalent to 0.004 per cent. copper.

#### VARIATIONS OF DELIVERIES.

Record of variations of deliveries of draughts from pipette in 1909-'10 in copper per cent.

Date.	Average difference in grams.	Copper per cent.
1909.		
May 6	0.0010	0.0017
13	0.0027	0.0047
20	0.0031	0.0054
27	0.0017	0.0030
Jun. 3	0.0025	0.0044
10	0.0017	0.0030
17	0.0032	0.0055
24	0.0012	0.0022
July 8	0.0040	0.0078
15	0.0044	0.0080
22	0.0036	0.0063
29	0.0026	0.0043
Aug. 5	0.0004	0.0007
12	0.0029	0.0046
19	0.0017	0.0030
26	0.0060	0.0100
Sep. 2	0.0008	0.0014
16	0.0081	0.0142
23	0.0018	0.0031
30	0.0005	0.0009
Oct. 5	0.0016	0.0028
14	0.0011	0.0020
28	0.0077	0.0135
Nov. 4	0.0023	0.0040
8	0.0022	0.0039
17	0.0040	0.0075
25	0.0074	0.0130
Dec. 2	0.0052	0.0091
9	0.0022	0.0039
16	0.0034	0.0060
23	0.0005	0.0009
30	0.0019	0.0035
1910		
Jan. 6	0.0008	0.0015
13	0.0029	0.0055
20	0.0005	0.0009
27	0.0012	0.0020
Feb. 3	0.0011	0.0019
17	0.0017	0.0030
24	0.0006	0.0011
Mar. 3	0.0011	0.0019
Average.	0.0026	0.0044

#### SOLUTION OF THE COPPER AND PREPARATION OF THE ELECTROLYTE.

The 80 grams in the 2000-cc. flask are treated with a cold mixture of 80 cc. sulphuric acid (sp. gr. 1.84), and 200 cc. nitric acid (sp. gr. 1.42) with 500 cc. of water. A standard solution of sodium chloride is added in sufficient quantity to precipitate the silver, care being taken to add less than 20 per cent. excess.

A bulbed condenser tube is placed in the neck before putting the flask on a plate which gradually heats the solution to boiling.

When but little of the ground drillings remain undissolved the solution is boiled gently for one hour.

Systematic examination of the residue left undissolved, by this treatment, has shown that the amount of copper retained in the residue rarely exceeds 0.001 per cent. in the case of normal brands of blister copper.

In the analysis of abnormal samples, bulky insoluble residues containing lead, tin or silica are separated at this point by filtration. The residues or precipitates are completely freed from copper by repeated fusions and precipitations.

When silver chloride is present in quantity sufficient to appreciably affect the volume of the solution, correction is applied to the copper result in accordance with a calculation based on the amount of silver as determined by the silver assay and the specific gravity of silver chloride.

When the solution in the flask has cooled for half an hour, water is added to a little above the 2000 cc. mark. During the addition, mixture of the water and solution is accomplished by giving the flask a rotary motion.

The flask is placed in a large tank containing water and allowed to remain until it becomes of the same temperature as the water and very close to that of the room. It is then removed to the level table, made up to the 2000 cc. mark by the addition of water from a burette, very thoroughly shaken, replaced in the tank and allowed to settle before pipetting.

Water flowing from the tank, through heavy walled rubber tubing, to the jacketed portion of the pipette and inflow tube, corrects the influence of the temperature of the room on the volume of the solution in the siphon and pipette.

Four portions, each representing two grams of the original ground drillings, are run off through the pipette into the glasses in which electrolysis is to take place.

The glasses (Fig. 5) are like hydrometer jars in shape, 6 $\frac{1}{2}$ " high and 2 $\frac{1}{6}$ " diameter with concave bottoms and have a capacity of 180 cc.

Two of the portions are reserved for use in case of irregularity occurring in the work upon the other two. Each portion is treated with 5 cc. of a saturated solution of ammonium nitrate and diluted to 125 cc. with water.

Ammonium nitrate, in the quantity added, has proved quite efficient in delaying the deposition of



Fig. 5.

arsenic and antimony until the electrolyte is completely freed from copper. The electrolyte, at this stage, contains about 3.7 cc. of nitric acid.

#### ELECTROLYSIS.

The positive electrode is a straight platinum wire extending to the bottom of the jar. The negative electrode is a cylinder  $1\frac{3}{4}$ " long, 1" in diameter, of 0.004" irido-platinum foil, all joints gold soldered, having a weight of about 12 grams and depositing surface of  $11\frac{1}{2}$  square inches. During electrolysis the jar is covered with split watch glasses.

Electrolysis is usually commenced at 5 P.M. with a current of 0.33 ampere per 100 sq. cm. which is kept constant until deposition is completed. In the morning the inside of the jar, the rods of the electrodes and the split watch glasses which cover the jar are rinsed with a spray from a wash bottle.

When deposition is completed, about 20 hours after the commencement of electrolysis, each electrode is quickly detached from the binding posts, the cathode plunged into cold water, then successively into three jars of 95 per cent. alcohol, shaken free of adherent drops and dried over a Bunsen flame for a few seconds after ignition of the film of alcohol.

The weighing of the foil plus the deposit is made with as little delay as possible.

Duplicate results rarely differ more than 0.02 per cent. The practice is to weigh each foil every two weeks and the difference from the previous weighing is rarely more than two-tenths of a milligram, the equivalent of 0.01 per cent. copper.

The foils are burnished when necessary.

The weights used are checked periodically against a set standardized by the Bureau of Standards at Washington.

For the weighing of the foils, a four-inch beam button balance fitted with wide bows is employed. With the full load of about 14 grams the balance is sensitive and accurate to one-twentieth milligram and will make one swing in eight seconds.

The six electrolytic circuits are connected with a conveniently arranged switch and rheostat board. By switch connection an ammeter can be thrown into circuit with any one of the systems.

At night, storage batteries supply the current which is kept constant by the factory watchman. During the day, while the batteries are being charged, the current is from the factory generator plant and its constancy is maintained by the analysts.

A uniform current is essential.

#### DETERMINATION OF THE AMOUNT OF COPPER LEFT IN SOLUTION AFTER ELECTROLYSIS.

After the electrodes have been removed, hydrogen sulphide is passed into one electrolyte of each sample in order to discover by the color of the precipitate

whether an abnormal amount of copper remains in solution.

The electrolytes, duplicates to those subjected to the above treatment, are combined, according to brand, evaporated to small bulk if necessary, neutralized and then slightly acidified with HCl. The retained copper is precipitated as sulphide and filtered off. The filter paper and contents are placed in a porcelain crucible, dried, ignited and the residue dissolved with little hot nitric acid.

Without removal from the crucible, the copper is determined by comparison of the shade of the ammoniacal solution with that of a similar solution containing a known amount of copper. Care is taken that similar conditions prevail when making the comparison. Correction is made for the small amount of copper so determined.

Those electrolytes from which the duplicates do not agree within 0.02 per cent. and such that retain copper equivalent to 0.02 per cent. are excluded from the above operations. The number of electrolytes thus rejected is very small, owing to active circulation and consequent uniformity of completion of deposition in jars with concave bottoms.

The average amount of copper retained in the electrolytes seldom exceeds the equivalent of 0.01 per cent.

#### CHARACTER AND PURITY OF THE DEPOSITED COPPER.

The ideal deposit, which can only be obtained by the electrolysis of a pure copper solution under the right conditions, is of a salmon-pink color, silky in texture and luster, smooth and tightly adherent.

The presence of even a small quantity of other metallic elements in the electrolyte is apt to modify these characteristics, either as a contaminant or by influencing the shape of the minute crystals that form the deposit.

A slightly spongy or coarsely crystalline deposit, although good in color and perfectly adherent, will invariably give a high result and is a condition to be guarded against quite as much as the deposition of impurity.

A loosely adherent deposit, caused either by too rapid deposition at the commencement or too low a current density at some period of electrolysis, usually shows a red tint and may give a high result on account of oxidation or a low result because of detachment of particles.

A darkly shaded deposit indicates the presence of impurity in greater or less quantity. If it is impossible to complete the deposition without this appearance the electrolyte must be purified.

Very impure copper is so exceptional in our practice that we will merely state, without going into detail, that, from such material bismuth, arsenic, antimony, selenium and tellurium are separated from the pipetted



portion by the addition of ferric nitrate and precipitation with ammonia.

Inasmuch as the deposited copper is never absolutely pure it is necessary that its appreciable impurity should be deducted from its weight. It is, therefore, a part of the general method to make a periodical complete analysis of the deposited copper from each brand of blister. The very small percentage of the impurities found becomes a correction to be applied to the analyses of samples of the corresponding brands.

#### IMPURITIES IN COPPER DEPOSIT IN DAILY WORK

150-200 grams of the deposited copper used in the case of each analysis:

Brand.	AgCl.	Ag.	As.	Sb.	Se and Te	Bi.	Pb.	Per cent. Total
A.	0.0046	0.0040	0.0018	0.0029	0.0029	None	.....	0.0162
		0.0100	Trace	0.0007	0.0270	"	.....	0.0377
		0.0085	0.0015	0.0003	0.0002	0.0017	.....	0.0122
		0.0130	0.0009	0.0011	None	0.0034	"	0.0184
B.	0.0057	None	0.0005	0.0016	0.0064	None	.....	0.0107
		0.0090	None	0.0014	0.0050	"	.....	0.0154
		0.0090	"	0.0013	0.0004	"	.....	0.0107
		0.0073	0.0006	"	0.0002	0.0022	None	0.0103
C.	0.0123	0.0004	0.0022	0.0040	0.0028	Trace	.....	0.0217
		0.0210	0.0012	0.0019	0.0027	0.0012	.....	0.0280
		0.0120	0.0010	0.0013	0.0013	0.0060	.....	0.0216
		0.0096	0.0041	0.0012	0.0022	0.0017	.....	0.0188
D.	.....	0.0120	None	0.0017	0.0048	0.0003	None	0.0188
E.	.....	0.0074	"	0.0011	0.0021	None	.....	0.0106
F.	.....	0.0115	0.0010	0.0020	"	"	.....	0.0045
G.	.....	0.0175	0.0030	0.0022	0.0034	"	.....	0.0261
H.	0.0123	0.0010	None	0.0016	0.0016	"	None	0.0165
I.	0.0262	0.0044	0.0014	0.0028	0.0010	"	.....	0.0358

#### METHOD FOR DETERMINING COPPER IN REFINED COPPER.

A "catch weight," approximately 5 grams of drillings, is placed in a beaker-shaped dissolving apparatus designed to hold a series of watch glasses. 10.5 cc. of nitric acid, 4.5 cc. of sulphuric acid and 35 cc. of distilled water are added and solution effected on a steam plate.

All possibility of loss is prevented by means of the watch glass traps (see Fig. 6).

After the dissolving glass is free from red fumes the watch glasses are rinsed, the electrolyte is made up to 200 cc. with distilled water, five grams of ammonium nitrate added and electrolysis carried on for 21 or 22 hours with a current of 0.47 ampere per 100 sq. cm.

The negative electrode is a platinum cylinder of 25 square inches surface. The anode is a spiral platinum wire.

The split watch glasses which cover the flask are rinsed with a spray from a wash-bottle four or five hours before the completion of electrolysis.

After electrolysis the exhausted electrolytes are combined and the amount of copper in solution, always

less than 0.01 per cent., estimated by the method previously described.

For the purpose of systematically checking the blister copper method of analysis, a standard sample is prepared from the borings of a single bar of furnace refined electrolytic copper.

The shavings from the surface of the casting are separated by hand-picking and rejected together with the fines passing through a 6-mesh screen.

The coarse, clean shavings are subjected to an analysis for copper according to the method just described, using 6 lots of 5 grams each, and also for oxygen and other impurities.

The following table gives the complete analysis of four separate samples of such standard copper:

	A.	B.	C.	D.
Cu + Ag	99.916	99.973	99.9600	99.97400
O	0.068	0.029	0.0400	0.03200
AS	.....	.....	0.0002	0.00015
SB	.....	.....	0.0004	0.00090
Se and Te	.....	.....	0.0002	0.00100
	99.984	100.002	100.0014	100.00805

These analyses are proof of the purity of the deposited copper.

Twice a week, in routine with the regular work, this standard is assayed by the same method which is employed for blister copper. The results are made items of permanent record and indicate, at once, any tendency to error on account of faulty manipulation or apparatus.

#### CONCLUSION.

In concluding this paper, it is to be noted that one proof of the accuracy of the method lies in the fact that, in the case of the standard copper, results by it agree exactly with those by the exceedingly accurate "five-gram method."

Up to the point of depositing the copper, the accuracy of each step of this method has been verified by experiment, but our experience, and what we have observed of the experience of others, shows that the tendency is to obtain results higher than truth in the process of electrolysis.

Too low a current density or excessive oxidizing power of the electrolyte may produce high results due to oxidation of the deposited copper, while too high a current density or deficiency of oxidizing power in the electrolyte, by causing the deposition of impurities, will have the same effect.

The conditions governing electrolysis must be fixed by rigid investigation.

The salient features of the method are summarized as follows:

The unusually large amount of 80 grams is taken for the purpose of reducing to a very low limit the error pertaining to the use of a sample composed of particles very dissimilar in size and value.

An automatic dividing pipette is employed for the sake of expedition and accuracy.

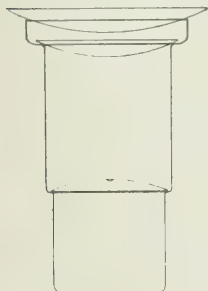


Fig. 6

\* Impurities in combined deposits.

Constancy of the volume of the assay solution is maintained during the operation of aliquoting by means of water of the same temperature as the solution running through the jacketed portion of the pipette from the tank in which the flask is immersed.

Error in weighing is minimized by the deposition of two grams of copper on an electrode of small area and weight.

With the object of preventing oxidation of the copper by the electrolyte, as high a current density is employed as is consistent with the formation of a smooth deposit.

Active circulation throughout the electrolyte is procured by electrolyzing in a glass having a concave bottom.

Account is taken of deposited impurities and correction is applied appropriate to the brands undergoing assay.

By the weekly testing of the accuracy of the delivery of the pipette and the twice-a-week assay of standard copper, the accuracy of the work is checked.

In developing the method to its present standard of excellence, I wish to acknowledge the assistance of all the laboratory staff who have contributed, but, more especially to Mr. William O'Gorman who has charge of copper determinations and Mr. F. A. Holbrook, formerly first assistant chemist.

I wish, also, to express appreciation to Mr. W. G. Derby, present first assistant chemist, for doing most of the work of preparing this paper and for reading it before the New York Section of the American Chemical Society.

## A RAPID METHOD FOR THE ELECTROLYTIC DETERMINATION OF COPPER IN ORES.

By R. C. BENNER

Received March 8, 1910.

When the greatest possible accuracy is desired in the determination of copper, recourse is had to the electrolytic method. The great disadvantages in this have been either the length of time it took to make the determination in case of the ordinary method; or (when the deposition is to be quickly made), the necessity of a special piece of complex apparatus, the rotating electrode, or a solenoid. Quite recently it has been found that it is possible, by means of the gauze electrode,<sup>1</sup> to deposit certain metals nearly as rapidly as with either of the pieces of apparatus mentioned. This gives an apparatus which is as simple and costs no more than that in ordinary use; and yet will give results with a rapidity nearly equal to those obtained with the more complicated and costly pieces.

The platinum electrode used in these determinations was corrugated and sand-blasted, cylindrical in shape,

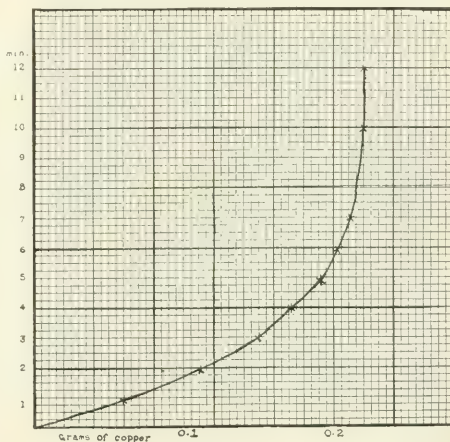
and about one inch in diameter by one and one-half inches long, made from fifty-two mesh wire gauze.

The accuracy was checked against C. P. copper foil, which had been proven to contain 100 per cent. copper by the ordinary electrolytic method. The copper foil was dissolved in three cc. of nitric acid (sp. gr. 1.4), diluted to seventy-five cc. with water and electrolyzed in from ten to fifteen minutes with a current of about ten amperes and four volts.

Cu taken.	Cu found	Volume of solution	Amperes	Nitric acid.	Time
0.1181	0.1181	75 cc	10-15	1 cc.	10
0.3586	0.3584	75 cc	10	3 cc.	12
0.2330	0.2332	75 cc	8-10	3 cc.	12
0.2142	0.2142	75 cc	8-10	3 cc	15
0.2374	0.2375	75 cc	8-10	3 cc.	15

The preceding results show that the accuracy is equal to that of the older method. The character of the deposit is all that could be asked for.

The rate of deposition under these conditions will be readily seen from the following results and a glance at the curve.



Cu taken.	Cu found.	Volume of solution	Amperes.	Nitric acid	Time
0.2203	0.0625	75	10	3	1
0.2203	0.1129	75	10	3	2
0.2203	0.1518	75	10	3	3
0.2203	0.1706	75	10	3	4
0.2203	0.1901	75	10	3	5
0.2203	0.2039	75	10	3	6
0.2203	0.2100	75	10	3	7
0.2203	0.2205	75	10	3	10
0.2203	0.2206	75	10	3	12

All but about seven and five-tenths per cent. is precipitated in the first five minutes, while it takes another five to complete the precipitation. This point is frequently overlooked, especially in technical work, and therefore gives rise to error.

*Process for Ores.*—From 0.5 to 1.0 gram of the ore, which contains none of the interfering elements, is dissolved in nitric or nitric and hydrochloric acids. When

<sup>1</sup> Stoddard, *J. Am. Chem. Soc.*, **31**, 385 (1909); *Chem. News*, **99**, 292.

aqua regia is used, or if lead is present, sulphuric acid is added and evaporation continued until the heavy white fumes of sulphuric anhydride are evolved. The excess of sulphuric acid is neutralized with ammonia and three cc. of concentrated nitric acid added.

Providing sulphuric acid is not added it is only necessary to concentrate to three cubic centimeters. In either case the solution is diluted to 75 cc., transferred to a tall battery beaker, without being filtered (if the residue does not settle it is better to filter) and the copper deposited by means of a current of 8 to 10 amperes and 3 to 4 volts. If the deposit is black or dark colored it is dissolved in nitric acid and redeposited in the same way. This redeposition is, as a rule, easier and quicker than filtering. The following results show the accuracy of this method on ores, as compared with those obtained by the older method.

#### RESULTS OBTAINED WITH THE GAUZE ELECTRODE

No. of sample.	Amount of ore taken.	Per cent. Cu in ore.	Copper found.
4.....	0.5003	0.0825	16.49
4.....	0.5003	0.0824	16.47
6.....	0.5003	0.0770	15.39
6.....	0.5003	0.0769	15.37

#### RESULTS OBTAINED BY THE ORDINARY METHOD

4.....	0.5000	0.0825	16.50
4.....	0.5000	0.0825	16.50
6.....	0.5000	0.0770	15.38
6.....	0.5000	0.0769	15.38

*Process for Slags.*—In case of slags and other low-grade material it is necessary to select a method of disintegration suited to the particular material in hand. Slags, which always give large quantities of gelatinous silica and contain low percentages of copper, give the most accurate results when disintegrated by means of nitric acid followed by hydrofluoric and sulphuric acids. After evaporation until heavy white fumes are evolved, the analysis is finished as in the process with ores. Redeposition is more frequently necessary with low-grade material than with high-, but in all cases it is more rapid, as well as more accurate, than filtering.

The following will illustrate the accuracy of the procedure:

#### DETERMINATIONS MADE WITH THE GAUZE ELECTRODE.

No. of ore.	Amount of ore taken	Copper found.	Per cent. Cu in ore.
13.....	1.0000	0.0060	0.60
13.....	1.0000	0.0059	0.59
13.....	2.0000	0.0123	0.61
11.....	2.0000	0.0103	0.51
11.....	2.0000	0.0101	0.50

#### DETERMINATIONS MADE BY THE ORDINARY METHOD.

13.....	2.0000	0.0121	0.60
13.....	2.0000	0.0121	0.60
11.....	1.0000	0.0051	0.51
11.....	1.0000	0.0050	0.50

Elements which interfere, and at the same time are likely to occur in copper ores, are arsenic, antimony, lead and bismuth. The separation of antimony and bismuth from copper was tried under the preceding conditions but without success. Lead, in such quan-

ties that it will deposit with the copper, is best removed as the sulphate. Arsenic, in small quantities, will not deposit with the copper, but in amounts about equivalent to the copper present begins to be deposited with the last of this. The following series of experiments, in which copper was deposited in the presence of varying amounts of arsenic, illustrates this point.

Arsenic taken.	Copper taken.	Copper found.
0.0605	0.2652	0.2648
0.1210	0.2751	0.2747
0.1815	0.2183	0.2183
0.1210	0.3038	0.3035
0.2420	0.2686	0.3106
.....	0.2028	0.2026

All these depositions were made under the usual conditions. From these results it is seen that arsenic, when present in amounts large enough to contaminate the copper deposited, can easily be removed by dissolving the deposited copper and reprecipitating under the same conditions as before. The removal of the interfering elements by chemical means can be accomplished by the following method:

The ore is disintegrated with nitric and hydrochloric acids, five or six cubic centimeters of sulphuric acid added and then it is evaporated until heavy white fumes of sulphuric anhydride are given off. It is now diluted to one hundred and fifty cubic centimeters with water, boiling to insure complete solution of the basic sulphate of iron (a few drops of hydrochloric acid are added if silver is present), filtered and washed with water containing a little sulphuric acid. The lead and silver remain on the filter paper. The filtrate is now heated to boiling and saturated with hydrogen sulphide, allowing the solution to cool during the process. The precipitated copper sulphide is filtered off and washed with water containing hydrogen sulphide. The precipitated sulphides are rinsed from the filter paper into a beaker using as little water as possible, warmed with a little colorless sodium sulphide to remove the antimony and arsenic and again passed through the same filter, being washed with water containing some sodium sulphide. Bismuth is now removed from copper by warming the mixed sulphides with a solution of potassium cyanide alkaline with ammonia. This dissolves the sulphide of copper leaving that of bismuth insoluble. The solution of the copper is boiled with nitric acid to destroy the potassium cyanide and electrolyzed in the usual manner.

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## THE EXACT DETERMINATION OF SULPHUR IN PYRITE AND MARCASITE.

By E. T. ALLEN AND JOHN JOHNSTON.

Received March 8, 1910.

Technical chemists have regarded the determination of sulphur in pyrite, which serves as the starting point in the manufacture of vast quantities of sul-



phuric acid, of very high importance. The fact is abundantly attested by the great body of literature which has been devoted to the subject. This has been well summarized by Lunge, who has himself made valuable contributions to it.<sup>1</sup> Lunge's well-known method, as formerly carried out, with a slow precipitation of the barium sulphate, gave results which were considerably too low. As since modified by the rapid precipitation suggested by Hintz and Weber,<sup>2</sup> it is more accurate, but, as we have elsewhere shown,<sup>3</sup> the results of the improved method involve a number of variable errors which compensate one another only partially. In the method which we have to propose, the results obtained under carefully regulated conditions are corrected for actual errors by methods which have been fully studied, and though it is less convenient in some respects than Lunge's method and lays no claim to rapidity, it should be of value as an umpire method.

Although the errors in the determination of pyrite and marcasite are chiefly the errors involved in the precipitation of barium sulphate from a solution of sodium sulphate and sodium chloride, very considerable errors may be involved in the grinding of the material.

*Oxidation of the Sulphides of Iron in Dry Grinding.*—It is well known that the sulphides of iron, especially marcasite, gradually oxidize when exposed to the atmosphere. We have frequently noticed a strong odor of sulphur dioxide on opening a bottle containing any of them, more particularly when finely ground. During the operation of grinding, oxidation appears to be accelerated, probably by the local heating in the disruption of particles.<sup>4</sup> The evolution of sulphur dioxide is not sufficiently rapid to be noticed in the grinding but, as shown below, ferrous sulphate is always found in the ground material. The data follow:

*Pyrite.*—A sample of pure pyrite from Elba was ground for an hour in the agate mortar of a McKenna ore-grinder. The product was washed on a filter paper and the iron and sulphur were determined in the soluble portion.

Fe = 0.0117 g.<sup>5</sup> equiv. to  $\text{SO}_4$  0.0200 g.  
 $\text{SO}_4$  found 0.0202 g.

Another portion of the same sample, ground 6 hours, yielded a water extract which contained:

Fe = 0.0253 g. equiv. to  $\text{SO}_4$  0.0434 g.  
 $\text{SO}_4$  found 0.0435 g.

*Marcasite.*—A sample of marcasite from Joplin, Mo., also ground six hours and extracted with water, gave:

<sup>1</sup> Report Int. Com. on Analysis, Subcommittee 9, 5th Int. Cong. Applied Chemistry, Rome, 1906, p. 399.

<sup>2</sup> *Z. anal. Chem.*, **45**, 31 (1906).

<sup>3</sup> *J. Am. Chem. Soc.*, **32**, 602.

<sup>4</sup> The ferrous silicates behave in a similar way. See *Mauzelius, Arsbok Sveriges Geologiska Undersökning*, 1907, No. 3. Hillebrand, *J. Am. Chem. Soc.*, **30**, 1120 (1908).

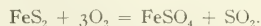
<sup>5</sup> On the assumption that the soluble iron exists wholly as ferrous sulphate.

Fe = 0.0079 g. equiv. to  $\text{SO}_4$  0.0136 g.  
 $\text{SO}_4$  found 0.0139 g.

*Pyrrhotite.*—A sample of artificial pyrrhotite containing only a little sulphur in excess of the ratio Fe:S = 1:1, gave on the same treatment:

Fe = 0.0057 g. equiv. to  $\text{SO}_4$  0.0098 g.  
 $\text{SO}_4$  found 0.0092 g.

These figures show plainly that ferrous sulphate is formed in grinding the sulphides of iron. The ground material yielded no oxide of iron when digested with 20 per cent. hydrochloric acid (conc. HCl diluted with an equal volume of water); ferrous sulphate and sulphur dioxide are therefore the only products of oxidation and the reaction may be represented by the equation



The weights of sulphide taken are not included in the above data, because it was found that a part of the oxidation in these experiments occurred during the washing. To eliminate this error, in the following experiments the ground material was washed in an atmosphere of carbon dioxide. The apparatus, enclosing a funnel with dry filter to which the ground material was transferred, was first exhausted by an ordinary water pump, and filled with carbon dioxide which had been freed from oxygen by heated copper. To remove oxygen more completely from the apparatus the process of exhaustion and filling with carbon dioxide was repeated. The sulphide was now washed with boiled water which had been cooled in carbon dioxide.

#### OXIDATION IN GRINDING PYRITE.

Time 1 h.			
Taken. Gram.	Fe in filtrate. Gram.	Equiv. to FeS <sub>2</sub> . Gram.	Per cent. FeS <sub>2</sub> oxidized.
4.11	0.0042	0.0090	0.22
5.77	0.0059	0.0126	0.22
Time 6 h.			
4.21	0.0211	0.0451	1.07
6.13	0.0317	0.0679	1.11

A mixture of 99 pts.  $\text{FeS}_2$  plus 1.3 pts.  $\text{FeSO}_4$  would be formed by the oxidation of 1 per cent. of the pyrite. Such a mixture contains only 53.02 per cent. instead of 53.45 per cent. sulphur. Thus when 1 per cent. of the pyrite is oxidized, the sulphur found in analysis should be 0.43 per cent. too low. This corresponds to a loss of  $0.43/0.53 = 0.8$  per cent. of the sulphur originally present. A six-hour grinding may perhaps be regarded as excessive, but it is probable that the time is not so important as the degree of fineness to which the material is reduced. The operation is manifestly one which is likely to vary considerably, differences of pressure on the pestle especially influencing the rate of oxidation. The above figures are not intended as an accurate measure of this rate, but are quoted merely to show that grinding causes oxidation, the errors from which must be considered

in exact work, especially when, as Treadwell directs, the material is ground as fine as possible.<sup>1</sup>

As a matter of fact fine grinding is not necessary in the method given below, except as it enables one to mix inhomogeneous material thoroughly. If the material is not sufficiently homogeneous, the extent of oxidation in the finely-ground sample should be determined in the way just indicated. As far as the analysis is concerned, one can use, perfectly well, material which will pass through a 20-mesh screen. When the sulphides are gently crushed to this size there is scarcely any oxidation as the following experiments serve to prove.

Perfectly bright pyrite from the interior of a solid lump, and therefore presumably free from oxidation, was gently crushed in a hard steel mortar and passed through a 20-mesh screen. 3.75 g. of the screenings were treated with boiled water in an atmosphere of carbon dioxide as above.

Fe in the filtrate = 0.0009 g. equiv. to 0.0019 g.  $\text{FeS}_2$  or 0.05% oxidized.

In a duplicate experiment, 4.61 g. gave:

Fe in the filtrate = 0.0010 g. equiv. to 0.0021 g.  $\text{FeS}_2$  = 0.05% oxidized.

*Preparation of Material for Analysis.*—The samples of the minerals which were used in the subsequent analyses were as pure as could be found. The marcasite was from Joplin, Mo., and the pyrite from Elba. They were further purified from oxidation products in order to obtain uniform samples, as well as to increase the certainty of the analytical determinations. It will of course be understood that such a procedure is not applicable to commercial work. To remove the oxidation products both samples were boiled with 20 per cent. hydrochloric acid until fresh portions of the reagent were no longer colored. They were then washed very carefully in an atmosphere of carbon dioxide. The washing was done first with 20 per cent. hydrochloric acid, then with boiled water cooled in carbon dioxide. The filters and their contents were now transferred to vacuum desiccators which had previously been filled with carbon dioxide. The desiccators were then rapidly exhausted, first by the water pump, then by the mercury pump to a pressure of 1 mm. of mercury or less. These samples were not absolutely homogeneous; each contained a little quartz, but so little that it was believed that any error occasioned by the lack of uniformity was less than the errors of analysis. The samples thus prepared were used for all the subsequent work. They were kept in vacuum desiccators and only exposed to the air long enough to take out portions for analysis.

*Determination of the Sulphur. a. Oxidation.*—To insure the complete oxidation of the sulphur with absolutely no loss, we employed the method of Carius. About 4 cc. fuming nitric acid entirely free from sulphur were used for the oxidation of half a gram of

sulphide. The sealed tube, containing the sulphide and reagent prepared in the ordinary way, was heated to 125° (maximum) over night.<sup>1</sup> The excess of nitric acid was removed after transferring to a beaker by evaporation to dryness on the steam-bath, the operation being several times repeated with concentrated hydrochloric acid. The beaker was covered with a watch glass so long as there was any danger of loss from spattering.

*b. Separation of the Iron.*—The sulphate of iron was cooled and brought into solution with water (no acid is necessary), diluted to about 300 cc. and precipitated with sodium carbonate solution (5 per cent. solution of  $\text{Na}_2\text{CO}_3$  is suitable) with constant stirring. Only a slight excess should be used. The addition of a few drops of ammonia makes the precipitation complete. The precipitate settles well after warming on the steam-bath. Sodium carbonate was used instead of ammonia, because, as will be explained farther on, the losses of sulphur are much increased when barium sulphate is precipitated from ammonium sulphate. The precipitate of ferric hydroxide was now filtered and washed; to insure the complete separation of sulphur it was redissolved in the least possible quantity of 20 per cent. hydrochloric acid, and the iron reprecipitated. The second filtrate and washings were kept separate from the first.

*c. Precipitation of the Sodium Sulphate by Barium Chloride.*—Each of the above filtrates was now brought to a volume of about 350 cc., either by dilution or evaporation as the case may require. The solutions were just acidified by hydrochloric acid, with the aid of a drop or two of methyl orange, then 2 cc. 2 per cent. hydrochloric acid (1 vol. conc.  $\text{HCl}$  diluted to 20 vol.) were added to each. In the precipitation of the barium sulphate, as will be explained farther on, the rate at which the reagent (22.5 cc. in quantity)<sup>2</sup> is added is all important. This is best regulated by attaching a capillary tip to the burette. The right diameter may be found by a few trials. The sulphate solutions were heated boiling hot and vigorously stirred while the reagent was allowed to flow down the side of the beaker. The precipitates were then left<sup>3</sup> to stand for about 18 hours, when they were filtered on paper and washed with hot water, till 25 cc. washings showed only the faintest opalescence with silver nitrate. Filtering and washing thus requires usually 1-1½ hours. The wet paper and precipitate were then heated *very slowly and carefully* in a platinum crucible, and finally, when the combustion was complete, ignited to constant weight.

<sup>1</sup> The glass tubes were heated in long steel bombs containing water, which served to compensate the pressure inside. This apparatus was at hand for other work and was used as a matter of convenience, but it was doubtless unnecessary.

<sup>2</sup> 0.5 g. pure  $\text{FeS}_2$  requires about 21 cc. of 10 per cent.  $\text{BaCl}_2$  solution, i. e., 10 g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 cc.  $\text{H}_2\text{O}$ .

<sup>3</sup> A Gooch crucible may be used, but precipitates formed in solutions containing very little acid are voluminous and inclined to clog the asbestos filter.

<sup>1</sup> "Quant. Anal.," trans. by Hall, p. 281.

*d. Errors in the Determination of Sulphur and their Corrections.*<sup>1</sup>—When a precipitation of barium sulphate is thus made from a solution of sodium sulphate, the weight of the precipitate is always too low. The authors have made a detailed study of the errors in the above case and of the methods of correcting them; these will here be briefly summarized:

1. The removal of nitrates is necessary, as has long been recognized; barium sulphate carries down nitrates and consequently the results are too high.

2. The solubility of the barium sulphate, of course, occasions a small loss, which is, however, much increased by free acid. With the quantity recommended, 2 cc. 2 per cent. HCl in a volume of 350 cc., and an added volume of 350 cc. washings, it amounts to 1–2 mg. only. It is not increased by the presence of sodium chloride. The solubility is determined in the usual way by evaporation of the filtrate and washings to dryness in a platinum basin, taking up with a little water and washing on a small filter, burning and weighing the precipitate.

3. All barium sulphate precipitates which have formed from alkali sulphates contain a number of impurities: barium chloride, alkali sulphate and “free” sulphuric acid, probably in the form of acid sulphate of the alkali metal. The quantity of alkali sulphate carried down by barium sulphate depends on many conditions, the most important of which are the quantities of free acid and alkali chloride present in the original solution. Barium sulphate from pure sodium sulphate carries down about 0.5 per cent. of the latter. This is more than doubled in the presence of much sodium chloride. The quantity may be determined by dissolving the weighed precipitate in 15 cc. concentrated sulphuric acid and pouring the cooled solution into about 300 cc. water with constant stirring. The precipitate and solution are heated some time and then filtered. The filtrate is carried to dryness in platinum under a hood with good draft and finally heated to redness. The residue is dissolved in a little water, filtered into a small tared dish, evaporated again to dryness, heated to redness, and weighed. This process does not extract all the sodium sulphate. Experiment has shown that the addition of 10 per cent. more to the quantity thus extracted will give the total amount with sufficient accuracy. If the analysis is made according to the directions in this paper, the quantity of sodium sulphate obtained by a single extraction in the precipitate should be close to 8.3 mgs. and the correction for it found by multiplying this quantity plus 10 per cent. by the factor  $(\text{BaSO}_4\text{--Na}_2\text{SO}_4)/\text{Na}_2\text{SO}_4$ , 5.8 mgs. If the iron is precipitated by ammonia the solution will, of course, contain ammonium sulphate and the barium sulphate precipitated from it will contain a considerable quantity of ammonium sulphate, which volatil-

izes when the barium sulphate is heated, thereby occasioning a loss considerably larger than that caused by the non-volatile sodium sulphate. Naturally, if corrections are to be made, they should, in the interests of accuracy, be kept as low as possible.

4. *The Loss of Sulphuric Acid by Volatilization.*—Barium sulphate which has been precipitated from solutions of any of the alkali sulphates contains some “free” sulphuric acid, or presumably, acid sulphate of the alkali metal. This acid is lost on heating, though the precipitate remains quite neutral. This remarkable fact has been fully substantiated by many experiments. The losses are much increased by two conditions—the presence of free acid and of alkali chloride, and will easily surpass one per cent. of the total sulphur if the quantity of both these substances is not carefully limited. There is another condition also that exercises an important influence on it, *viz.*, the speed of precipitation. If this be rapid (ca. 10 secs.), the quantity of “free” sulphuric acid is lowered and under certain conditions practically vanishes. The determination of the volatility loss is best made by heating in a platinum boat, inside a platinum combustion tube, a precipitate formed under the same conditions as the one which is weighed. With the outlet of the combustion tube is connected a Liebig potash bulb containing 10 cc. water and 1 cc. perhydrol free from sulphur. When the loss is comparatively large, two bulbs are needed and the quantity of perhydrol is increased. As a precaution it is well to rinse the combustion tube with water after the experiment. With the conditions recommended, the error from this cause is only 0.6 mg. for 2 g. precipitate, corresponding to 0.03 per cent. of the total sulphur.

5. *The Occlusion of Barium Chloride.*—All freshly precipitated barium sulphate contains some barium chloride. This amounts to only about 0.15 per cent. in precipitates which are slowly formed in sodium sulphate solutions; it introduces no error in the determination, because the chloride is transformed by the occluded sodium sulphate during ignition into barium sulphate and hydrochloric acid, and all but a trace of the chloride is thus eliminated. If the precipitation is rapidly made, the amount of chloride in the precipitate is much greater and several tenths of a per cent. remain in the precipitate after heating to redness. Thus another correction is necessitated.

6. *Effect of the Time of Standing on the Composition of Barium Sulphate Precipitates.*—When precipitates are left to stand in the liquid from which they are thrown down, they slowly change in composition approaching somewhat nearer to pure barium sulphate. The process is accelerated to some extent by heating, though the addition of a large excess of barium chloride has no effect. In exact determinations of sulphur, therefore the barium sulphate should not be filtered

<sup>1</sup> For a full discussion of this subject see *J. Am. Chem. Soc.*, **32**, 604-6



at once for in that case the losses from both occlusion and volatilization are higher. 18 hours is a practical time to allow before filtering. The corrections given in this paper imply this condition. The authors have found that the corrections discussed in the preceding paragraphs are quite constant when the prescribed conditions are strictly adhered to. In the analyses which follow, the results have therefore been corrected by the use of constants previously determined under similar conditions.

One analysis each of pyrite and marcasite was made exactly according to the method described above; two others were made by a slightly modified method in which magnesium oxide<sup>1</sup> was used to precipitate the iron. This method has the advantage that the results obtained by it, require only a solubility correction, for magnesium sulphate is carried down by barium sulphate in almost negligible quantity. This error, which lowers the result slightly, is practically compensated by the presence in the precipitate of a little barium chloride (0.10–0.15 per cent.). The volatility loss is a mere trace. The method has the disadvantage that the precipitated iron (or probably the excess of magnesium oxide in it) retains sulphur persistently. Three precipitations were in fact required to recover all the sulphur.

## ANALYTICAL DATA I.

*Pyrite*.—a. Sodium carbonate method:

0.5208 g. pyrite gave .....	2.0184 g. BaSO <sub>4</sub>
Corr. for solubility <sup>2</sup> .....	2.0
Corr. for occlusion of Na <sub>2</sub> SO <sub>4</sub> ..	5.8
Corr. for volatility .....	0.6
Total corrs. ....	0.0084
	2.0268 g. = 53.46% S.

## b. Magnesium oxide method:

0.4685 g. pyrite gave .....	1.8227 g. BaSO <sub>4</sub>
Corr. for solubility .....	0.0036 <sup>3</sup>
	1.8263 g. = 53.53% S.

*Marcasite*.—a. Sodium carbonate method:

0.5005 g. marcasite gave .....	1.9328 g. BaSO <sub>4</sub>
Corr. as under pyrite (a) .....	0.0084
	1.9412 g. = 53.28% S.

## b. Magnesium oxide method:

0.5026 g. marcasite gave .....	1.9476 g. BaSO <sub>4</sub>
Corr. as under pyrite (b) .....	0.0036
	1.9512 g. = 53.33% S.

A few determinations for the sake of comparison have been made by Fresenius' and by Lunge's method both somewhat modified. The results have also been corrected for the errors already discussed. Even after correction, however, we do not regard the results on coarse material as equal in accuracy to those just given.

*Corrected Analyses by Fresenius' Method.*—It is

<sup>1</sup> The reagent was carefully freed from lime and sulphur.  
<sup>2</sup> The correction for solubility is 1 mg. for each of the two solutions. Both were brought to a volume of 350 cc. so that the same correction might be used for both.

<sup>3</sup> The correction obtained experimentally is multiplied by 3 because three precipitations, and therefore three solubility corrections, were necessary.

commonly directed in this method to pulverize the sulphide before fusing with sodium carbonate. But since we have shown that this operation may involve a considerable error, the following analyses were made on the 20-mesh material. Only in details was there any change in the ordinary procedure. For the sake of certainty in correction, we fused with a mixture of 4 pts. sodium carbonate and 1 pt. sodium nitrate (instead of nitre).<sup>1</sup> Six grams of the mixture were used. The fusion was heated in a platinum crucible, first over a burner and finally for a few minutes over the blast; meanwhile, it was protected from the sulphur of the flame by a good-fitting asbestos board. The cooled fusion was extracted with water and the precipitate well washed. The iron was redissolved and reprecipitated as described under the first method. Both filtrates were brought to about 350 cc. and acidified as there described; the remainder of the procedure is also the same in every way. In correcting the weight of the precipitate it must be remembered that the sulphate was precipitated from a solution containing close to 6 g. of sodium chloride, the amount yielded by 6 g. of the above fusion mixture. The presence of this salt makes a considerable difference in the composition of the precipitated barium sulphate and therefore in the corrections to be applied to it. The occluded sodium sulphate amounts on the average to 17.4 mg. (for 2 g. precipitate) and the correction for it (after an allowance of 10 per cent. for incomplete extraction) 12.2 mg.; the average volatility loss is 5.9 mg., while the solubility loss remains unchanged, 0.2 mg. The sum of these corrections is 20.1 mg.<sup>2</sup>

## ANALYTICAL DATA II.

a. 0.5031 g. pyrite gave .....	1.9346 g. BaSO <sub>4</sub>
Sum of corrs. as above .....	0.0201
	1.9547 g. = 53.37% S.
b. 0.4815 g. marcasite gave .....	1.8421 g. BaSO <sub>4</sub>
Corrs. as above .....	0.0201
	1.8622 g. = 53.13% S.
c. 0.4758 g. marcasite gave .....	1.8194 g. BaSO <sub>4</sub>
Corrs. as above .....	0.0201
	1.8395 g. = 53.11% S.

*Corrected Results by Lunge's Method.*—The weighed quantity of sulphide crushed to 20-mesh size was allowed to stand over night in the cold with 10 cc. of a mixture of 3 vol. conc. nitric acid and 1 vol. conc. hydrochloric acid. The solution was then evaporated on the steam bath, first without, then several times with hydrochloric acid to remove the nitric acid. The remainder of the analysis was exactly like the method proposed and described above.

<sup>1</sup> The correction constants were determined on precipitates of barium sulphate which were thrown down in solutions containing only sodium salts.

<sup>2</sup> The correction constants were determined on precipitates formed in the presence of 5 g. and 10 g. NaCl respectively. The occlusion number is practically identical for both. The volatility losses are 5.2 mg. and 8.8 mg. respectively; by interpolation we obtain 5.9 mg. for 6 g. NaCl.

## ANALYTICAL DATA III.

a	0.5100 g pyrite gave	1.9659 g. BaSO <sub>4</sub>
	Corrs. previously given, L.....	0.0084
		1.9743 g. = 53.18% S.
b	0.5315 g. marcasite gave	2.0417 g. BaSO <sub>4</sub>
	Corrections as above.....	0.0084
		2.0501 g. = 52.99% S.
c	0.5127 g. marcasite gave	1.9722 g. BaSO <sub>4</sub>
	Corrections as above.....	0.0084
		1.9806 g. = 53.07% S.

## CORRECTED RESULTS

	Pyrite.	Marcasite.
Authors' method	53.53	53.33
	53.46	53.28
	53.49 Av.	53.30 Av.
Fresenius' method modified.....	53.37	53.13
		53.11
		53.12 Av.
Lunge's method modified	53.18	52.99
		53.07
		53.03 Av.

The concordance in the duplicates given above shows that the determinations were carefully done. We ascribe the lower results by Fresenius<sup>1</sup> and Lunge's methods to a loss of sulphur during oxidation. In the last determination of the sulphur in marcasite, a little unoxidized sulphur was in fact noticed. The loss probably would not have occurred had the material been finely ground, but if fine grinding is resorted to another error is introduced. The Carius method of oxidation avoids both errors.

**Control of Sulphur Determinations.**—For the sake of control, 5-g. portions of both pyrite and marcasite were subjected to qualitative analysis. Except for a trace of copper in the marcasite only silica was found: 0.04 per cent. in the pyrite, and 0.20 per cent. in the marcasite. As a final check on the accuracy of the sulphur determination, it seemed desirable to determine also the amount of iron in portions of the same purified pyrite and marcasite.

## DETERMINATION OF THE IRON.

1. **Volumetric.**—About 0.25 g. substance was decomposed in the usual way with 10 cc. of a mixture of 3 parts conc. HNO<sub>3</sub> to 1 part conc. HCl. The excess of acid was gotten rid of by evaporating with sulphuric acid, first on the water bath and finally over a free flame, until voluminous white fumes appeared. The residue was dissolved and diluted with water to about 200 cc., nearly neutralized with ammonia,<sup>2</sup> reduced with sulphur dioxide,<sup>3</sup> and titrated as usual with permanganate solution, in the presence

of sufficient added sulphuric acid. A weight burette was used throughout. The permanganate solution was standardized by means of sodium oxalate ("nach Sørensen," obtained from Merck), which had been previously heated for an hour at 240°.<sup>1</sup> As a result of several closely agreeing determinations, 1 g. KMnO<sub>4</sub> solution = 0.002633 g. Fe. A number of blank experiments were performed, and the amount of permanganate used up in them, varying from 0.05 to 0.07 g., was subtracted from the quantity used in titration. The amounts given below have been corrected in this way.

- (a) 0.2682 g. pyrite required (1) 47.62 g. (2) 47.54 g. permanganate.  
 (b) 0.2682 g. pyrite required (1) 47.53 g. (2) 47.63 g. permanganate.

The percentage of iron from these four analyses is therefore: 46.75, 46.67, 46.66 and 46.75; the mean value is 46.72 per cent. Fe, whereas FeS<sub>2</sub> requires 46.55 per cent. Fe.

- (a) 0.2576 g. marcasite required 45.62 g. permanganate.  
 (b) 0.2719 g. marcasite required (1) 48.01 g. (2) 48.06 g. permanganate.

The percentage of iron from these three analyses is 46.63, 46.49 and 46.54; the mean value is 46.55 per cent. Fe.

2. **Gravimetric.**—The first determinations of the iron were made by the gravimetric method. To our surprise, they were all unaccountably high. As a result of some study it may be said that determinations by this method are invariably too high if certain precautions are not taken, and in view of the importance of the method our experience is here included.

If the precipitation is done in platinum by pure ammonia, the results leave little to be desired. In the following determinations, the sulphide was dissolved in aqua regia, the excess of acid removed by evaporation, the residue dissolved and filtered into platinum and twice precipitated by pure ammonia. In this precipitation the details given by Lunge were followed, viz., the liquid was heated to a temperature of 40–50°, the ammonia added and the whole then heated to boiling. In the second precipitation macerated filter paper was added to the solution to make the ignited precipitate more porous and to insure the complete reoxidation of any magnetite formed in the burning.<sup>2</sup> The second precipitate was thoroughly washed by the aid of the pump. The ammonia used was purified by distillation, the washed vapors being absorbed by water in a ceresin bottle; 25 cc. of this ammonia gave no weighable residue.

- Pyrite (a) 0.5272 g. gave 0.3504 g. Fe<sub>2</sub>O<sub>3</sub>; Fe = 46.46%.  
 (b) 0.5344 g. gave 0.3557 g. Fe<sub>2</sub>O<sub>3</sub>; Fe = 46.53%.

The mean value, 46.49, agrees very closely with the theoretical number for FeS<sub>2</sub>, viz., 46.55 per cent. Fe.

<sup>1</sup> This heated salt (as was afterwards observed) reacted very slightly alkaline, due to the formation of a trace of sodium carbonate, but cannot account for the fact that the volumetric results are somewhat higher than the final results obtained by precipitation with ammonia. Any other impurity in the oxalate, if neutral to permanganate, would of course make the percentage of iron too high.

<sup>2</sup> W. F. Hillebrand, *Bull. U. S. G. S.* **305**, p. 88.

<sup>1</sup> The possibility that a loss of SO<sub>2</sub> may be caused by the contamination of the precipitate by iron should also be considered. In Fresenius' method, a little iron is dissolved when the fused mass is leached by water. This iron would probably be carried down by the barium sulphate as ferric sulphate, which would lose sulphur on ignition. See Jannasch and Richards, *J. pr. Chem.*, **39**, 321; E. A. Schneider, *Z. physik. Chem.*, **10**, 425, 1892.

<sup>2</sup> In presence of much free acid the reduction is incomplete. Private communication from W. F. Hillebrand and R. S. McBride.

<sup>3</sup> In every case complete reduction was assured by testing a drop of the liquid with thiocyanate.

Marcasite: a. 0.5028 g. gave 0.3444 g.  $\text{Fe}_2\text{O}_3$ , Fe = 46.49%  
 b. 0.5209 g. gave 0.3471 g.  $\text{Fe}_2\text{O}_3$ , Fe = 46.57%

The mean value is 46.53% Fe.

*A Common Error in the Gravimetric Determination of Iron.*—From several private communications, as well as from our own experience, it appears that the results obtained from gravimetric determinations of iron are generally too high, and by an amount which may well be 2 per cent. of the total iron present. Nevertheless, there appear to be no specific references to this fact in the literature. The first two analyses of pyrite made by us gave identical results, 47.45 per cent. Fe, which are certainly much in excess of the true value. These analyses were performed exactly as described above, except that the iron was precipitated in beakers of Jena glass by means of ammonia, the purity of which had not been recently controlled. This was confirmed by a number of analyses of a solution of ferrous ammonium sulphate, in which the conditions of oxidation and precipitation were varied; the results, however, varied only from 0.004590 to 0.004623 g. Fe per g. solution, as compared with 0.004524 obtained volumetrically.

It was now found by evaporation in platinum that the ammonia left a residue; this ammonia had been redistilled not long before; nevertheless, from 25 cc. of it (about the amount used in a double precipitation), insoluble residues weighing 3.0–3.2 mg., were obtained. Now, since the usual weight of a precipitate of  $\text{Fe}_2\text{O}_3$  is from 300–350 mg., it is evident that this source alone may be responsible for an error of as much as 1 per cent. of the total iron. The ammonia was therefore subjected to redistillation and the washed vapors absorbed by water in bottles of (1) ordinary glass, (2) Jena glass, and (3) ceresin (such as are used for hydrofluoric acid).

Direct tests made one month later showed the amount of residue from 25 cc. ammonia from each of these to be respectively: (1) 0.7 mg.,<sup>1</sup> (2) 0.4 mg., (3) 0.0 mg. The ceresin bottle is thus entirely satisfactory;<sup>2</sup> the others have been attacked by the ammonia to a slight extent, but sufficient to produce an error in the determination of iron, which is not negligible.

That impurity in the ammonia is not responsible for the whole error is evident from the following analyses, in which the iron was precipitated twice in Jena glass beakers by means of pure ammonia: (a) 0.5048 g. pyrite gave 0.3383 g. ppt., whence Fe = 46.85 per cent. (b) 0.5239 g. marcasite gave 0.3514 g. ppt., whence Fe = 46.89 per cent.

<sup>1</sup> The distillation of this ammonia was conducted with very great care. The much larger amount of impurity given above is not to be referred to any special lack of care during the distillation, and that such an amount is not exceptional is shown by the uniformly high results of a number of analyses in which other samples of ammonia were used. However that may be, the figures represent real amounts, which may be encountered by anyone who does not specially control the purity of the ammonia he uses.

<sup>2</sup> Such bottles are used to some extent for this purpose. The magnitude of the errors caused by ammonia which has been kept in glass does not appear to have been generally recognized.

Thus the error is still fully 0.6 per cent. of the total iron. Further, special experiments undertaken with the purpose of tracing down this source of error showed that the use of glass beakers was responsible, and that by discarding glass entirely, and by making the precipitations in platinum vessels, satisfactory results are obtained.

The definitive determinations of iron in pyrite and marcasite were made under these conditions, and as we have seen, correct results were obtained. It is evident that it is necessary to guard against these sources of error whenever ammonia is used as a precipitant; they may exert a specially large influence in the determination of aluminum, on account of its low atomic weight and of the fact that it is frequently determined by difference.

If it is necessary to determine both iron and sulphur in the same sample, the use of sodium carbonate for the precipitation of the iron is advisable on account of larger errors otherwise involved. Experience has shown that it is safer to add the sodium carbonate slowly, and in dilute solution (in order to diminish occlusion), and that it may sometimes be necessary to make more than one subsequent precipitation with ammonia, in order to obtain precipitates free from all foreign material.

COMPLETE ANALYSES OF PYRITE AND MARCASITE

	Pyrite.	Marcasite.
Fe.....	46.49 <sup>1</sup>	46.53 <sup>1</sup>
S.....	53.49 <sup>1</sup>	53.30 <sup>1</sup>
$\text{SiO}_2$ .....	0.04	0.20
	100.02	100.03

We have selected the gravimetric results for iron as nearer the truth; if the volumetric numbers are used, the summations become 100.25 for pyrite and 100.05 for marcasite.

*Comparison of Authors' Method with that of Hintz and Weber.*—We have elsewhere shown that the method of Hintz and Weber, though a great improvement on those which preceded it, depends on a compensation of variable errors. The following figures (their best) give an idea of the accuracy.<sup>2</sup>

Assistant I.	Assistant II.
48.25	48.15
48.62	48.41

The variations in the work of each analyst are: I, 0.37 per cent., and II, 0.26 per cent., of the pyrite, or 0.7 per cent. and 0.5 per cent. of the total sulphur. Our own results show variations of 0.07 per cent. and 0.05 per cent. of the sulphide, = 0.13 per cent. and 0.10 per cent. of the total sulphur. These are the results obtained by using Carius' method in the oxidation; the results of the other methods, although they indicate a loss of sulphur, show equal uniformity in the determination of the sulphur present.

*Application of the Method to Other Insoluble Sulphides.*

<sup>1</sup> Average of two determinations.

<sup>2</sup> Z. anal. Chem., 45, 44 (1906).



—Although we have not tried the method proposed in this paper in the analysis of other sulphides, the principles which we have discussed, *viz.*, the error involved in the grinding of sulphides, the method of oxidation and the corrections for barium sulphate precipitates, would appear to be of perfectly general application. In the case of sulphides like those of antimony and bismuth in which not all the sulphur would be in soluble form after oxidation, an excess of sodium carbonate would be required to transform it all into sodium sulphate, and the excess of sodium carbonate, of course, would have to be subsequently changed into sodium chloride, which, as we have seen, increases the errors due to occlusion and volatility. The method, however, is still applicable, though the errors would have to be determined for each special case.

#### SUMMARY.

It has been shown that when the sulphides of iron are ground for analysis, they suffer partial oxidation to sulphur dioxide and ferrous sulphate. If they are finely pulverized this error is not negligible; it may be reduced to 0.05 per cent. by gentle crushing to 20-mesh size, which is sufficiently fine for the proposed method of analysis. Inhomogeneous material, such as would be met with in commercial work, would have to be pulverized for the purpose of accurate sampling. In that case, the error could be determined by washing a weighed portion of the powder with boiled water in an atmosphere of carbon dioxide, and determining the iron in the washings; the operation is rather exacting on account of the readiness with which the moist sulphide oxidizes.

In the proposed method, the sample is oxidized in sealed tubes, according to Carius; this avoids all possible loss of sulphur. Lunge's and even Fresenius' method gave in our hands lower results, a fact which we attributed to a loss of sulphur during oxidation, occasioned by the use of coarse material, or perhaps, in Fresenius' method, to the presence of iron in the barium sulphate.

The iron is removed by two precipitations with sodium carbonate. The object of this is to avoid ammonium salts, which cause much larger losses of sulphur. In precipitating the barium sulphate several conditions must be carefully followed, *viz.*, the free acid must be reduced to a small measured quantity, and the precipitation must be made at a measured rate. These two conditions are necessary because they determine the composition of the precipitate, which is not pure barium sulphate, while the first determines also the loss by solubility.

In every case, three corrections must be made on the weight of the barium sulphate precipitate: (1) a correction for solubility of the precipitate, which depends on the volume of the solution and the quantity of free acid it contains; (2) a correction for the occlusion of sodium sulphate by the precipitate, which

depends on many conditions, but chiefly on the quantity of alkali chloride originally present in the solution; (3) a correction for a certain amount of free sulphuric acid lost on ignition. This is not due to any sort of decomposition of the barium sulphate, but to the presence in the precipitate of "free" sulphuric acid, probably in the form of sodium acid sulphate. The most important conditions affecting this error are the quantity of free acid and of sodium chloride in the solution, and the rate at which the precipitation is made; an increase of either acid or sodium chloride increases the error; a rapid rate of precipitation decreases it, but so far as our experiments have been carried, there is not in this case sufficient uniformity in the results to allow of satisfactory corrections. Constants may be used in making all these corrections if the conditions set down are carefully followed, but otherwise they must be determined by methods given in the body of this paper. These corrections have been fully worked out by studying the precipitation of pure sodium sulphate under various conditions. The analytical data on the sulphides appear the more certain since they have been controlled by complete analyses of material which gave both positive and negative evidence of nearly theoretical purity.

The sum of the errors in this method, apart from that involved in the grinding, should not be over 0.2 per cent. of the total sulphur. The extreme variation in our own analyses was less than 0.15 per cent. and the agreement was equally good when other methods of oxidation were combined with our own scheme of precipitation and correction. Hintz and Weber's method for sulphur in pyrite is the best hitherto described; its essential features are oxidation according to Lunge, and a rapid precipitation of the barium sulphate. Their own best published results, however, vary from 0.5 per cent. to 0.7 per cent. of the total sulphur.

Incidentally, it was learned that the precipitation of iron by ammonia involves much larger errors than have generally been supposed, if, as is customary, the ammonia is kept in glass bottles and the precipitation is made in glass beakers. The same error would affect the precipitation of alumina and other similar oxides.

GEOPHYSICAL LABORATORY,  
CARNEGIE INSTITUTION OF WASHINGTON,  
WASHINGTON, D. C., March 3, 1910.

[CONTRIBUTION FROM NEW MEXICO AGRICULTURAL EXPERIMENT  
STATION.]

#### EXAMINATION OF CANDELILLA WAX.

By R. F. HARE AND A. P. BJERREGAARD.  
Received March 1, 1910.

*Description of the Plant.*—The wax here reported upon is found coating the entire surface of a plant that grows wild in the semi-arid regions of northern Mexico and southern Texas. The plant is reported

to be abundant over large areas of this section, where it occurs as bunches of leafless, reedlike stems 2 to 4 feet high and from  $\frac{1}{4}$  to  $\frac{1}{2}$  inch in diameter. The common name given to the plant by the Mexicans is candelilla. According to competent botanical authorities it is in all probability *Euphorbia anti-syphilitica*.<sup>1</sup>

*Preparation of the Wax.*—The stems of this plant received by us from Mexico were tied in bundles, thrown into a vessel of cold water and weighted down to prevent them from floating. The water was then heated to boiling, when the wax melted and rose to the surface. After cooling, the impure cake of wax which floated on the water was removed and dried. In this condition it was of a dark brown color, due

90 per cent. benzene mentioned above was found to be an excellent solvent when hot. The hot solution from all of these solvents gelaťinized to a pomade-like mass on cooling. Upon slow evaporation from dilute solution it formed white cauliflower-like masses. An examination under the microscope showed no crystals or polarization effect in either the pomade mass or the solid formed from slow evaporation of the dilute solution. The wax obtained in the manner described above had 0.64 per cent. ash which was practically pure calcium carbonate. Some of the physical and chemical constants of candelilla wax are given in the following table along with those of carnauba wax, beeswax and chinese insect wax as given by Lewkowitsch.

CONSTANTS OF WAXES  
Candeilla wax.

	Original state.	Rendered ash-free.	Carnauba wax.	Beeswax.	Chinese insect wax.
Specific gravity at 15° C.	0.9825		0.990–0.999	0.964–0.970	0.926–0.970
Melting point	67–68° C.		85–86° C.	61.5–64.4° C.	80.5–83° C.
Solidifying point	64.5° C.		80–81° C.	60.5–62.8° C.	80.5–81° C.
Acid value in mg. KOH	12.4	17.4	4–7	16.8–21.2	...
Saponification value in mg. KOH	64.9	84.1	79–95	90–98	80.5–93
Iodine absorption	36.8	33.6	13.5	7.9–11	...
Unsaponifiable matter, per cent	91.17	84.2	55	52.56	...
Ash, per cent.	0.34	00.0	0.43	...	...
Fatty acids, per cent.	6.57			...	...
Refractive index	At 71.5° C. 1.4555		At 80° C. calc. to 40° C. 1.471	At 62° C. calc. to 1.4455	...

to presence of minute fragments of bark and other foreign matter. The wax was purified by dissolving in hot chloroform, filtering hot and removing the chloroform by evaporation over the water bath. It was then further purified by dissolving in a boiling mixture of three parts absolute alcohol and two parts of 90 per cent. benzene. This solution was filtered hot and the solvents again removed by evaporation over the water bath. The product thus obtained was a pale grayish yellow, opaque solid, the opacity being caused by a small amount of water. When the sample was melted and dried, it lost 6.36 per cent., became translucent and assumed a brownish yellow color. The amount of wax obtained in this form amounted to about 2.5 per cent. of the partially dried plants.

*Examination of the Wax.*—The hardness of this wax on the mineral scale was found to be between 1 and 2. It was harder and more brittle than beeswax, but not so hard and brittle as carnauba wax. It had the odor of beeswax, and this is much more pronounced when the wax was warmed. It was but slightly soluble in cold ether, chloroform, alcohol, turpentine, gasoline, carbon bisulphide and acetone, but readily soluble in all of these when hot. Mixing these solvents was not usually found to improve the solubility when cold, but the mixture of alcohol and

It will be seen from the table that the specific gravity, melting point, solidifying point, acid value, and refractive index of candelilla wax is intermediate between beeswax and carnauba wax. The saponification value is lower than either. The iodine absorption (Hanus method) and per cent. unsaponifiable matter are both much greater than either.

The unsaponifiable matter did not increase in weight on attempted acetylation. It was a dull brittle waxy mass of a dark ochre-yellow color soluble in hot absolute alcohol, chloroform and acetic anhydride. The whole solution solidified on cooling to a white pomade-like mass similar to that of the original wax. The unsaponifiable matter dissolved in hot gasoline, and in a hot mixture of chloroform and acetic anhydride, and in both cases the solution remained clear on cooling. Concentrated sulphuric acid added drop by drop to the latter solution caused a purplish red color with faint yellowish green fluorescence. The color did not change on standing but the fluorescence became olive colored. Dissolved in chloroform, cooled and an equal volume of concentrated sulphuric acid added, a yellow color resulted. After shaking and settling the upper layer was very pale yellow and the sulphuric acid layer dark ochre colored. Dissolved in acetic anhydride and a drop of 60 per cent. sulphuric acid added a pale violet pink color appeared (Liebermann-Storch reaction). It dissolved completely in warm concentrated sulphuric acid with a reddish brown

<sup>1</sup> A description of this plant is found in Dr. Candel's *Prodromus*, 15, Pl. 2a, 69.

color. On dilution and standing several hours the solution became pale lavender, while a dark olive-green semi-solid floated on top. This sample of unsaponifiable matter began to soften at about  $75^{\circ}\text{C}.$ , but was not sufficiently liquid to flow at  $125^{\circ}\text{C}.$  It contained considerable ash not readily soluble in water, but soluble in dilute acid. The ash was found to contain some lime.

The low saponification value obtained by us was probably not due to insufficient saponification, as the wax was digested for five hours in very strong solution of caustic soda prepared by dissolving sodium in alcohol admixed with an equal volume of purified gasoline.

The wax acids separated from the soaps obtained in the saponification were dark brown, softer than the original wax and free from ash.

The wax was prepared ash-free by dissolving in boiling glacial acetic acid and pouring the hot filtered solution into an equal volume of cold dilute hydrochloric acid. After thoroughly washing the wax obtained in this manner with water, some of its chemical constants were determined and are given in the table with those of the wax as examined in the original state. The cause for the differences there shown is not apparent.

The dried and filtered commercial wax yielded on combustion the following average of two closely agreeing determinations:

Carbon, per cent .....	80.30
Hydrogen, per cent .....	12.69

A sample of sugar cane wax analyzed by Dumas<sup>1</sup> was found by him to contain 81 per cent. carbon and 14.16 per cent. hydrogen. He regarded this substance as an alcohol of the formula  $\text{C}_{24}\text{H}_{50}\text{O}$ .

It will be observed that the candelilla wax is somewhat similar to the cane wax in its ultimate composition. The probabilities are, however, that candelilla wax like carnauba wax is a mixture of an alcohol, an ester, and some free fatty acid. If, however, an alcohol is present it should be possible to acetylate the unsaponifiable matter. We attempted the acetylation by the Benedict-Lewkowitsch method, but obtained negative results.

## CONSTANTS OF CHINESE WOOD OIL.

By ADOLPH KREIKENBAUM

Received March 11, 1910

Chinese wood oil is a comparatively new article in general commercial use. It is now very much used in the manufacture of varnishes.

In the following work only the results of the determinations of the constants are given and a discussion of the analytical features added. The literature offers comparatively little definite regarding the constants of the oil and at most a considerable con-

fusion of figures together with a wide range given for the various constants.<sup>1</sup> In some cases individual analyses upon some sample of unknown or doubtful source is submitted and in other cases it is evident that a confusion of products is at fault in that Japanese wood oil and Chinese wood oil have been classed alike,<sup>2</sup> being in the opinion of the writer two separate and distinct products. This opinion is based upon references found in literature<sup>3</sup> and not from original knowledge. The values given by Lewkowitsch in the table of constants for Chinese wood oil are evidently some Chinese wood oil and some Japanese wood oil figures. The values given for the specific gravity of Chinese wood oil by Lewkowitsch himself agree with the results obtained in this work. It seems that a distinction should be observed between the two products, Chinese wood oil and Japanese wood oil by all chemists, because the two oils are evidently separate and distinct substances, and the indiscriminate interchange of the figures of the two oils under one synonym *Tung* oil causes an unnecessary confusion and hardship for the analytical chemist, who may be compelled to make use of published data for reference.

The value of the work embodied in this article and the results obtained and submitted in their entirety are due to the fact, that the determinations of the constants have been made upon exact and carefully taken average samples of large commercial shipments of *Chinese* wood oil. This has been done for two years and the samples examined thus show how uniform a product the Chinese wood oil of commerce is. The investigation also reveals the fact that each constant varies but very slightly with the exception of the free acid value. The complete figures for each sample will tell their own story best.

All of the following specimens of the oil represent an average of regular commercial shipments. Several fluid ounces of the oil were taken from each barrel, emptied into a single container, mixed thoroughly and preserved in a tightly stoppered bottle filled close up to the cork and the bottles preserved in a dark, cool cupboard near the floor. More specific details are given directly under the various specimens. The column marked *Age* in the analysis tables indicates the time elapsed between the receipt of the shipment and the date the particular analysis was made.

### Number 1.

Shipment received October, 1907. Represents average of about 100 barrels which bore the same brand. Filled one-gallon can full, tightly stoppered; kept in cool place. October, 1908, transferred some of this

<sup>1</sup> Tech., *Chemistry and Technology of Mixed Paints*, ed. 1907, p. 99, *Chem. Engr.*, **9**, 186.

<sup>2</sup> *Analyst*, **23**, 113, 118.

<sup>3</sup> *Ibid.*, **23**, 113, 118; Kametaka, *J. S. C. I.*, **27**, abstract of *J. Coll. Science Imp. Univ. Tokyo*, 1908, p. 25; Lewkowitsch, *Chem. Tech. and Anal. Oils, Fats and Waxes*.

<sup>1</sup> Quoted by Browne in *Bull.* **91**, Louisiana Experiment Station.



oil into a 16-oz. bottle and filled nearly to the cork. Determinations made from this bottle sample:

Spec. grav.	0.9416	15.5 15.5	Pycnometer.	Age 13 mos	Remarks.
"	"	15.5 15.5	"	2 yrs	Poured from bottle without shaking
Free acid 4.8 mgs. KOH.				13 mos	
Sapon No.	192.2 191.5	191.8		24 "	
Iodine.....	172.4 170.8	171.6	Hübl	15 hrs. 13 "	Hübl solution 6 days old.
"	170.0 171.8	170.9	"	3 " 13 "	Hübl solution 7 days old
"	168.9 169.2	169.0	"	18 " 16 "	
"	165.5 164.5	165.0	"	3 " 16 "	
"	170.0 169.5	169.7	"	4 " 17 "	
"	170.1 170.2	170.1	"	18 " 21 "	
"	212.2 209.4	210.8	Hanus	30 min 16 "	
"	209.7 206.6	208.1	"	30 " 16 "	
"	208.3 209.0	208.6	"	30 " 12 "	
"	196.0	196.0	"	30 " 12 "	

#### Number 2.

Received October, 1907. Average of 100 barrels, the lightest colored ones found in a total lot of 600 barrels, coming from different shippers. One-gallon can full retained. Transferred some of the oil to bottle October, 1908, from which determinations were made.

Spec. grav.	0.9427	15.5 15.5	Pycnometer.	Age 13 mos	Remarks.
"	"	15.5 15.5	"	24 "	Poured from bottle without shaking
"	"	15.5 15.5	"	24 "	Bottle shaken. oil well mixed.
Free acid 2.3 mgs. KOH.				13 "	
Sapon No.	190.7 190.5	190.6		24 "	
Iodine.....	173.0 172.2	172.6	Hübl	15 hrs. 13 "	Hübl solution 6 days old.
"	168.3 171.3	169.8	"	18 " 16 "	
"	163.3 164.6	163.9	"	3 " 16 "	
"	169.2 169.7	169.4	"	4 " 17 "	
"	169.6 169.1	169.3	"	18 " 21 "	
"	196.6 197.8	197.2	Hanus	30 min 12 "	
"	194.3 196.1	195.2	"	30 " 13 "	
"	199.5 204.4	201.9	"	30 " 16 "	
"	212.8 207.6	210.2	"	30 " 16 "	
"	207.8	207.8	"	30 " 24 "	

#### Number 3.

Received October, 1907. Average of 400 barrels darkest colored oil from a total of 600 barrels. One-gallon can of the oil retained. Transferred to bottle October, 1908.

Spec. grav.	0.9436	15.5 15.5	Pycnometer.	Age 24 mos	Remarks.
Free acid 3.3 mgs. KOH.				13 "	From 1-gal can half full, exposed to air 1 year.
Sapon No.	192.0 191.6	191.8		24 "	From original 1-gal. can half full.
Iodine	168.5 169.5	169.0	Hübl	18 hrs 16 "	
"	163.9 165.1	164.5	"	3 " 16 "	
"	169.5 169.0	169.2	"	4 " 17 "	
"	172.0 171.3	171.6	"	20 " 21 "	
"	195.3 197.7	196.5	Hanus	30 min 12 "	
"	200.4 202.4	201.4	"	30 " 16 "	

#### Number 4.

Received October, 1907. Average of 20 barrels marked with a certain brand. Light color. Sample kept in one-quart can in dark, cool cupboard near floor. Can about half-full. Transferred into bottle October, 1908. Bottle completely filled.

Spec. grav.	0.9454	15.5 15.5	Pycnometer.	Age 24 mos	Remarks
Free acid 1.7 mgs. KOH.				13 "	First year in 1 quart can half full; second year 1 1/2 inch air space in bottle.
Sapon No.	190.9 190.5	190.7		24 "	
Iodine.....	162.8 163.1	162.9	Hübl	3 hrs. 17 "	
"	166.9 166.9	166.9	"	4 " 17 "	
"	169.9 170.9	170.4	"	20 " 21 "	
"	192.7 196.1	194.4	Hanus	30 min. 13 "	
"	193.2 197.8	195.5	"	30 " 17 "	

#### Number 5.

Received September, 1908. Average of 88 barrels. Filled 16-oz. bottle and preserved like the rest in dark, cool cupboard.

Spec. grav.	0.9414	15.5 15.5	Pycnometer	Age 12 mos
Free acid 4.5 mgs. KOH.				10 days
Sapon No.	191.2 191.4	191.3		12 mos.
Iodine	165.3 168.0	166.6	Hübl	3 hrs. 5 "
"	168.8 169.5	169.1	"	4 " 5 "
"	173.7 172.0	172.8	"	20 " 10 "
"	196.1 195.9	196.0	Hanus	30 min. 1 "
"	197.3 191.2	197.3	"	30 " 5 "
"	204.1	197.6	"	30 " 5 "

#### Number 6.

Received October, 1908. Average of 400 barrels. Filled some into bottle at once and preserved as usual.

Spec. grav.	0.9411	15.5 15.5	Pycnometer.	Age	
				16 days	
Free acid	5.3 mgs. KOH.			14 "	
Sapon. No.	191.6 191.9	191.7		12 mos.	
Iodine.....	169.3 169.6	169.4	Hübl.	3 hrs.	4 "
" .....	171.4 171.9	171.6	"	4 "	4 "
" .....	170.1 170.1	170.1	"	18 "	9 "
" .....	192.2 192.6	192.4	Hanus	30 min.	1 day
" .....	200.0 192.6	200.0	"	10 "	2 "
" .....	199.9	196.2	"	30 "	4 mos.

## Number 7.

Received October, 1908. Average of 100 barrels.  
Light color. Bottle sample preserved at once.

Spec. grav	0.9406	15.5 15.5	Age.	Remarks.
			2 days.	From bottle.
" "	0.9401		7 days	From 1/2 gal. can of same lot.
" "	0.9407		12 mos.	From bottle.
Free acid	6.1 mgs. KOH.		2 days	
	6.3	"	5 "	
Sapon. No.	190.5 190.7	190.6	12 mos.	
Iodine.....	168.7 170.2	169.4	Hübl	3 hrs. 4 mos.
" .....	173.4 173.3	173.3	"	4 " 5 "
" .....	170.3 170.0	170.1	"	18 " 9 "
" .....	205.3 205.9	205.6	Hanus	30 min 2 days
" .....	204.5 208.1	206.3	"	30 " 2 "
" .....	201.3 191.0	196.1	"	" 4 mos.
" .....	188.8 189.0	188.9	"	30 " 5 "
" .....	201.0 197.2	199.1	"	" Bromine in excess. Linseed, 187.1.

## Number 8.

Received June, 1909. Average of 249 barrels.  
Oil stood in one-gallon can open to air for two weeks before bottle sample was transferred.

Spec. grav.	0.9413	15.5 15.5	Age.
			2 mos.
Free acid	7.0 mgs. KOH.		2 "
Sapon. No.	190.0 189.7	189.8	4 "
Iodine.....	170.7 170.7	170.7	Hübl 20 hrs. 1 "
" .....	170.4 170.4	170.4	" 5 " 3 "

## Number 9.

Received June, 1909. Average of 200 barrels.  
Oil left in open pail nine days before bottle sample was transferred.

Spec. grav	0.9413	15.5 15.5	Age.
			3 mos.
Free acid	7.1 mgs. KOH.		3 "
Sapon. No.	190.6 190.5	190.5	3 "
Iodine.....	171.8 171.5	171.6	Hübl. 18 hrs. 1 "
" .....	173.1 173.1	173.1	" 5 " 3 "

## Number 10.

Received September, 1909. Average of 500 barrels.  
Filled into bottle at once.

Spec. grav.	0.9412	15.5 15.5	Age.
			1/2 mo
Free acid	2.4 mgs. KOH.		
Sapon. No.	190.8 190.4	190.6	1/2 "
Iodine.....	171.6 167.9	171.6	Hübl 7 hrs. 1/2 "
" .....	167.9 168.6	167.9	" 3 " 1/2 "
" .....	168.6 168.6	168.6	" 4 " 1/2 "

The results of this work indicate quite conclusively that the Chinese wood oil of commerce is a very uniform product. The constants vary but little. Summarizing the results there are obtained the following figures for the constants:

Specific gravity	15.5 15.5	by pycnometer 0.941
Free acid	1.7-7.1	average 4.4 mgs. KOH
Sapon. No.		average 190.9
Iodine No.	Hübl	average 170.4%.

The specific gravity of the fresh oil as received is practically 0.941. The minimum observation was 0.9401. In contact with air the specific gravity of the oil increases. Sample 4, which was in contact with much air for 2 years, gave at the end of that period 0.9454 and is the maximum figure obtained; others increased in a less degree. All determinations were made with the pycnometer. The Westphal balance, which gives accurate results upon such liquids as turpentine, benzine, alcohol etc., gives results 1 to 2 points in the third decimal too low when used for linseed oil or Chinese wood oil.

The free acid varied from a minimum observation of 1.7 to a maximum of 7.1 mgs. KOH, with an average of 4.4 for the ten samples.

The saponification number is 190.9, being the average of ten figures, minimum observation 189.8, maximum 191.8.

The iodine number proved to give interesting results, in the first place by giving such uniform results with the Hübl method and giving figures differing from those usually assigned to the oil in literature, and secondly, because the Hanus method was found inapplicable to Chinese wood oil. As a rule, the working of each iodine solution used, whether Hübl or Hanus, was tried for its action and result upon a sample of acid-free linseed oil kept for that purpose. The usual iodine number obtained for the linseed oil sample was 183-184 and the Chinese wood oil results were between 169-171 for these solutions. When the result on the linseed oil reached 185, the Chinese wood oil (see sample 7) showed 173. The Hübl solutions were from 12 to 48 hours old when used, except in the cases where stated otherwise. It can safely be said that the iodine number by the Hübl method is quite uniform in the neighborhood of 170 and age has had practically no effect on it. A three-hour absorption is insufficient, a four-hour absorption giving in most cases almost complete results, assuming 18 hours as standard. For the 18-hour absorption the minimum was 169.0, maximum 173.1.

The average of all Hübl iodine absorptions between 4 and 20 hours is 170.4. The 3-hour absorptions gave an average of 166.9 on 8 determinations, with a minimum of 162.9 and a maximum of 170.9. The 4 hour absorption shows an average of 169.7 on 8 determinations with a minimum of 168.6 and a maximum of 173.3. Two 5-hour absorptions gave 170.4 and 173.1. One 7-hour absorption gave 171.6. It can be assumed from the results of this work and upon the strength of it recommended that a 6- to 7-hour absorption will in all cases give a complete iodine absorption by the Hübl method. The results show that no further remark is necessary than that the Hanus method is not available for Chinese wood oil, although each Hanus solution gave results with the linseed oil sample, which agreed closely with Hübl determinations upon the same, this being a check test nearly always made to prove that the Hanus solution was not at fault.

It is my sincere hope to see a complete research made upon Chinese wood oil, so that the figures, which I submit here, will be verified and that all might be known, which good investigation will bring out, and that we become more enlightened about this most curious of vegetable oils. Further work in confirmation and extension of these results will be taken up by coöperation with other investigators.

CHEMICAL LABORATORY.  
THE GLIDDEN VARNISH CO.,  
CLEVELAND, O., February 16, 1910.

### GAMBOGE.

By F. O. TAYLOR.

Received March 10, 1910.

Of all the resins more commonly used there is none whose ordinary adulterations are more easy to detect than those of gamboge; nevertheless, we find that not only in the powdered state but also in the form of pipes or lumps it is largely adulterated. The adulteration of powdered resins is to be expected, but when the detection of adulteration is so simple a matter as with gamboge, one would imagine that at least more obscure methods of adulteration would be pursued. Such, however, seems not to be the case. For the purposes of this examination, fifteen samples of gamboge were obtained from a variety of sources, eight of these were powdered and seven were either pipes or broken lumps. The appearance of the powdered samples varied from an orange color to lemon-yellow, while of the seven unpowdered samples, five were of first-class appearance and two were considerably lighter in color than a good quality of gamboge should be, one of these being in form of pipe and marked "Saigon Gamboge." The examination of gamboge for adulterations as published in pharmaceutical literature has been chiefly confined to the examination for starch and almost exclusively to the powdered

form. Eberhardt<sup>1</sup> records his results in the examination of a number of samples of gamboge for starch and states that in several years' experience he had failed to discover a powdered gum that would not show at least a slight test for starch; in none of the samples of pipe gamboge did he discover any traces of starch. However, Daniel Base, in a paper before the Maryland Pharmaceutical Association,<sup>2</sup> states that he found, by means of a microscopical examination, a number of samples of gamboge adulterated in this manner, but attributes some of the adulteration to the use of dextrin instead of starch.

The present examination included the percentage of ash, alcohol-soluble matter, acid value and test for starch, the results of which will be found recorded in the table following:

TABLE I.

Sample Number	Starch Test	Per cent ash	Per cent alcohol-soluble	Acid value.
1	Trace (under 1%)	1.0	79.05	91.6
2	Marked	6.93	61.3	67.7
3	None	0.65	76.15	80.2
4	Very marked	11.00	39.25	56.3
5	Trace (faint)	0.69	77.0	85.8
6	Heavy	1.91	57.6	67.7
7	Very marked	6.76	61.0	73.3
8	Trace (under 1%)	1.02	60.1	64.9
9	Very marked	0.93	52.95	80.5
10	None	0.45	84.0	95.8
11	None	0.54	77.4	85.8
12	None	0.32	82.0	88.6
13	Marked	0.71	60.3	73.3
14	None	1.26	74.9	81.6
15	Heavy	0.70	49.95	64.9

*Starch Test.*—The U. S. P., Eighth Revision, includes no test for the presence of starch in gamboge, differing in this particular from the U. S. P., 1890. This was probably done with the supposition that gamboge in pipes, which is the only variety official, is not adulterated with starch. This is unfortunate, as out of seven samples of this character which were examined, two were markedly contaminated with starch, and in such a manner that it was evidently an intentional adulteration. The test given in the U. S. P., 1890, is sufficiently delicate for all practical purposes and is easily applied. Eberhardt (v. s.), while admitting the delicacy of this test, has proposed another based on the destruction of the starch granule with caustic alkali (which at the same time dissolves the gamboge resin), the precipitation of the resin and neutralization of the liquid with acid, and the testing of the filtrate with iodine. This test has the advantage of giving the blue color of starch iodide instead of the green color which appears when this blue is mingled with the yellow of the gamboge. In every case I have used the former U. S. P. test, which will, without difficulty, detect much less than one per cent. of starch.

Not one of the powdered samples showed but a trace of starch. In number 5 this was faint, in num-

<sup>1</sup> *Amer. Jour. Pharm.*, 1896, p. 371.

<sup>2</sup> *Ibid.*, 1900, p. 189.



bers 2 and 8 larger but still under one per cent. while in the others the amount of starch was very marked, some indications of the comparative amounts being given by the method of wording of the table. Microscopical examination revealed rice starch in every case except number 4, which contained cornstarch. In the two unpowdered samples, numbers 13 and 15, the starch had evidently been mixed with the melted resin so that part of it was converted into a soluble form, for upon shaking the powder made from these with water, without heat, the presence of starch was distinctly indicated by iodine. The powder made from the remaining samples of pipe gamboge showed absolutely no trace of starch. The cause of the slight trace of starch in some powdered gamboge, so small that it is evidently not an intentional adulteration, has been considered by Eberhardt, but no definite conclusion was arrived at. I have no additional suggestions to offer regarding this, but the fact remains that practically all samples of powdered gamboge will show at least a trace of starch.

*Ash.*—The U. S. P. requires gamboge to contain not more than three (3) per cent. of ash, but a first-class sample of gamboge comes well below this and the limit could be lowered. But one of the samples of the pipe or lump gamboge had an ash higher than 0.75 per cent., and this one (number 14) was due to the presence of some traces of fine gravel, evidently there as an accidental contamination. A large amount of the ash in numbers 2 and 7 were due to the presence of a considerable amount of fine sand, and the extraordinary quantity in number 4 was caused by the presence both of sand and a marked quantity of lead chromate, an adulteration unique in my experience, and yet one which might be expected. Both gamboge and lead chromate being used as pigments, it is no more than natural to expect that the gamboge intended for use as a pigment would, if adulterated at all, be sophisticated by the addition of the cheaper pigment of similar color (lead chromate), which is at the same time a make-weight for the lighter gamboge. Every sample of powdered gamboge with an ash above one (1) per cent., contained visible traces of sand under the microscope, but the amount was so small that it could scarcely have been used intentionally. It is possible that the gamboge might have been powdered in a ball-mill with stone balls, which would account for the traces of sand. This is the more reasonable when it is remembered how easily powdered gamboge is electrified, so, for the purpose of powdering it, stone would be preferable to metal.

*Alcohol Solubility.*—The U. S. P. requires gamboge to contain not more than twenty-five (25) per cent. insoluble in alcohol. This was obtained by treating one (1) gram of powdered resin with one hundred (100) cc. of alcohol, letting stand over night with occasional shaking, filtering through a tared filter,

and weighing the washed and dried residue. Six out of the fifteen samples are above this standard, while a seventh (number 14) is so slightly below that it may properly be counted within the standard. Of these seven, two were powdered samples and the remaining five were the five best appearing unpowdered samples. Below this standard the remaining samples ranged in solubility from 61.3 to 39.25 per cent.

*Acid Value.*—The U. S. P. makes no requirements for acid value, but various observers have made record of this analytical value of gamboge, and the values assigned range between 70 and 90 for unpowdered samples. Von Schmidt and Erban, A. Kremel, and Beckurts and Brüche<sup>1</sup> record acid values on alcoholic extracts of gamboge, but these are not comparable to the results we give. Dieterich<sup>2</sup> in the examination of seven samples pipe gamboge obtained acid values from 71.45 to 86.46, and for the powdered gamboge about 110, the higher value for the powdered variety being due to the presence of rosin. The acid value was determined by the method suggested by Dieterich, digesting one (1) gram of resin with one hundred (100) cc. of alcohol on a steam-bath for fifteen minutes in a reflux condenser, adding fifty (50) cc. of water and cooling before titration. The titration is carried out with some difficulty because of the orange colored solution and the consequent lack of sharpness in the end-point reading. The following method may also be used, and is, I believe, preferable, for it enables the very rapid determination of both alcohol solubility and acid value at the same time.

Two (2) grams of gamboge are digested under a reflux condenser with exactly 150 cc. of alcohol for not less than fifteen minutes, the solution cooled and seventy-five (75) cc. (representing one (1) gram of resin) filtered off through a dry tared filter. This 75 cc. is used for titration of the acid value, which is made direct on this solution, and the filtration is continued so that the insoluble residue may be finally collected on the filter and weighed. This reduces the time for the determination of alcohol solubility to a few hours at most and in the acid value titration gives results agreeing with those obtained by Dieterich's method. This was proved by comparison of this method with Dieterich's on a number of the above samples; the results as a whole, however, had been originally determined by Dieterich's method, and as such they are recorded. The acid value of the samples whose alcohol solubility was up to standard ranged from 80.2 to 95.8. One other acid value above 80 (number 9) had quite a low alcohol solubility, which, in connection with the fact that a large amount of starch was present, indicated colophony. Other acid values ranged downward from this to 56.3.

<sup>1</sup> 'Analysis of Resins.' Dieterich pp. 292 and 293

<sup>2</sup> *Ibid* p. 204

*Comparison of Acid Value and Alcohol Solubility.*—The comparison of these data is instructive, and from it we may obtain a better idea of gamboge than from either alone. If we take the seven samples whose ash and alcohol solubility are up to standard, and arrange them in the order of their acid value, we will have a table as below.

Sample No.	Acid value.	Alcohol solubility.
10.....	95.8	84.0
1.....	91.6	79.05
12.....	88.6	82.0
11.....	85.8	77.4
5.....	85.8	77.0
14.....	81.6	74.9
3.....	80.2	76.15

The alcohol solubility, it will be noted, varies in direct proportion to the acid value with a considerable degree of accuracy, excepting number 1, and this, a powdered sample, appears to contain a small amount of colophony, so that though the alcohol solubility is lower than number 12, yet the acid value is higher. The samples of pipe gamboge, however, will excellently bear out this proportional relationship. If now we arrange the remaining samples in the same manner, we will have a table as shown below, from which we may draw conclusions regarding the samples which are adulterated with colophony.

Sample No.	Acid value.	Alcohol solubility.
9.....	80.5	52.95
7.....	73.3	61.0
13.....	73.3	60.3
2.....	67.7	61.3
6.....	67.7	57.6
8.....	64.9	60.1
15.....	64.9	49.95
4.....	56.5	39.25

Sample number 9 being heavily adulterated with starch is also undoubtedly adulterated with colophony. Sample number 2 in all probability contains colophony and with more certainty number 6. Number 8, while possibly containing colophony, is by no means as certain as any of the others. The remaining samples may be considered wholly free from this adulteration.

#### SUMMARY.

Out of the fifteen samples examined, only six are unquestionable, while a seventh offering some grounds for suspicion is yet so good as to be acceptable for ordinary use. Thus we find six out of eight powdered samples and two out of seven samples of pipe or broken gamboge, so heavily adulterated that there would be no question about their rejection for pharmaceutical use. Starch is found in large quantity in seven instances, and in addition to this, sand is present with evident intention in three instances. Number 8 is very low in alcohol solubility and acid value, though containing but a trace of starch; the ash is low, hence the adulterant must be some non-starchy, organic body, whose identity was not determined. Numbers 2 and 3 are interesting by reason of the fact that number 2, a powdered sample, was supposed to be made by powdering number 3. The

difference between the two is obvious. Sample number 4 appeared to be of excellent quality upon superficial examination, but proved to be decidedly worse than any other. Starch had been added to a considerable extent, and then to increase the weight some sand was put in, and to correct the light color produced, a small quantity of lead chromate was added. This adulteration has already been referred to, and I can but add that, while somewhat ingenious, it was so crude that its detection was easy. While the use of starch or sand as an adulterant simply decreases the strength of the gamboge, the presence of lead chromate goes further and adds the poisonous action of the lead salt, so causing the gamboge to become not merely inefficient but dangerous.

The alcohol solubility as required by the U. S. P. is, for a test of this character, unusually good for detecting adulteration, and the standard of the U. S. P. needs no change. The ash requirement might well be lowered so that it should read "not to exceed one per cent." The acid value is not essential to detection of most of the adulterated gamboge, but might be added. Lastly, 'y all means a starch test should be required, and I would suggest that it be worded so as to exclude any gamboge which shows more than a faint green color upon the addition of iodine to a powdered sample which has been boiled with water and subsequently cooled.

LABORATORIES OF PARKE, DAVIS AND CO.

## THE DETERMINATION OF SODIUM CHLORIDE IN MILK.<sup>1</sup>

By PAUL POETSCHKE.

Received February 17, 1910.

The addition of sodium chloride to milk is sometimes practiced with the object of increasing the density and ash content of watered samples. Having had occasion to examine numerous samples of milk for the presence of added sodium chloride, the author has devised a method which not only shortened the time required for this determination but also gave results which are more accurate than direct incineration in a platinum dish. It is customary to estimate chlorine in milk by incineration in a platinum dish, dissolving the ash in nitric acid, and proceeding with the determination of chlorine by Volhard's method. The fact that a loss of chlorine occurs even when the ignition is carried on at temperatures much below those at which chlorides become volatile is well known. This loss appears to be due to the formation of acid products during the ignition, and the loss of chlorine increases with the proportion of organic matter to chlorine. The addition of sodium carbonate prevents this loss, if the proportion of sodium carbonate is five per cent. of the organic matter present.<sup>2</sup> When a large number

<sup>1</sup> Read before N. Y. Section, February, 1910.

<sup>2</sup> Davis, *J. Soc. Chem. Ind.*, **20**, 98 (1901)

of samples are to be examined, considerable time is required in the ashing, especially if sodium carbonate is added, and it becomes necessary to employ quite a number of platinum dishes. Since the presence of copper and those metals whose salts are colorless (with exception of mercury) do not influence the accuracy of Volhard's method, it appeared possible to secure a proper solution for the determination of chlorine in milk by clarification with copper sulphate and sodium hydroxide. The preliminary results given in Table I and II indicated the possibility of applying this method.

TABLE I.

RESULTS EXPRESSED IN GRAMS OF SODIUM CHLORIDE PER 100 CC.					
Sample No.	44.145	44.146	44.147	44.310	44.311
Sodium chloride by direct ashing.....	0.168	0.162	0.162	0.198	0.198
Sodium chloride by ashing with sodium carbonate.....	0.178	0.162	0.175	0.207	0.207
Sodium chloride by author's method .....	0.180	0.167	0.183	0.208	0.210

TABLE II.

RESULTS EXPRESSED IN GRAMS OF SODIUM CHLORIDE PER 100 CC.							
Sample No.	(1)	(2)	(1) plus 0.1000 gram NaCl per 100 cc.	(1) plus 0.2000 gram NaCl per 100 cc.	(2) plus 0.1000 gram NaCl per 100 cc.	(2) plus 0.2000 gram NaCl per 100 cc.	(2) plus 0.3000 gram NaCl per 100 cc.
Sodium chloride by direct ashing.....	0.197	0.164	.....	.....	.....	.....	.....
Sodium chloride by ashing with sodium carbonate.....	.....	0.171	.....	.....	.....	.....	.....
Sodium chloride by author's method.....	0.198	0.176	0.293	0.399	0.286	0.385	0.482
Added sodium chloride found.....	.....	.....	0.095	0.201	0.110	0.209	0.306

## METHOD OF CARRYING OUT THE DETERMINATION

## Solutions Required.

1. Ammonium thiocyanate. A tenth-normal solution.
2. Copper sulphate. Dissolve 34.639 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water and dilute to 500 cc.
3. Ferric indicator. A cold saturated solution of ferric alum in water, to which enough nitric acid is added to cause disappearance of the brown color. Three cc. of this indicator are used for all titrations.
4. Nitric acid. An approximately 5 *N* solution free from lower oxides of nitrogen.
5. Silver nitrate. A tenth-normal solution.
6. Sodium hydroxide. A half-normal solution.

## DETERMINATION.

Twenty-five cubic centimeters of the carefully mixed sample are measured into a 200 cc. graduated flask, diluted with 125 cc. of water, 10 cc. of copper sulphate and 8.8 cc. of sodium hydroxide added. The mixture is diluted to the mark, mixed by inverting the flask ten to twelve times, at the same time shaking gently. It is then poured on a dry, folded filter 19 cm. in diameter and the filtrate collected in a dry flask. The funnel is kept covered with a clock glass and the neck of the flask in which the filtrate is received is loosely stoppered with a plug of cotton to minimize evaporation. The filtrate should have an acid reaction and contain a slight excess of copper. To

100 cc. of the filtrate 5 cc. of nitric acid and an excess of silver nitrate are added, together with 5 cc. of ether<sup>1</sup> which causes the silver chloride to readily coagulate and settle. The silver chloride is now filtered off and after the addition of ferric indicator to the filtrate, the excess of silver nitrate titrated with ammonium thiocyanate. From the amount of silver nitrate required, the amount of sodium chloride is calculated.

*Notes.*—In order to secure a clear filtrate after clarification, the sodium hydroxide is added gradually while shaking the flask containing the diluted milk and copper sulphate. After diluting to the mark, the contents of the flask are mixed by inverting the flask and shaking gently, since violent shaking caused the filtrate to come through turbid and the filtration to be slow. The first portion of filtrate is rejected since it is usually turbid, the dry flask being placed under the funnel when the filtrate becomes clear. Usually the filtrate is clear after a few cubic centimeters have run through. On the addition of nitric acid a turbidity usually develops which does not interfere with the determination, and for this reason the filtrate from the silver chloride is sometimes slightly turbid.

If great accuracy is desired, normal twentieth solutions of silver nitrate and ammonium thiocyanate should be used, and corrections applied for the volume occupied by the precipitated fat and proteids. The correction for volume of precipitate can be obtained by the method of double dilution. For this purpose two dilutions are made, one in the regular way as already given and another in which the volume is completed to 100 cc. The volume of precipitate is twice as great in proportion in the 100 cc. as in the 200 cc. flask. The following example shows the method of calculation.

Per cent. sodium chloride by weight found by diluting to 100 cc. = 0.171.

Per cent. sodium chloride by weight found by diluting to 200 cc. = 0.169.

$0.171 - 0.169 = 0.002$  (half the error in the higher result).

$0.171 - (0.002 \times 2) = 0.167$  corrected percentage of sodium chloride.

The volume as precipitate is calculated as follows:

$0.171 : 0.167 : 100 : x = 97.66$  which is the volume of solution in the 100 cc. flask. Therefor the volume of precipitate is 2.34 cc. The results given in Table III indicate that when the volume is made up to 200 cc., the correction of volume of precipitate is well within the ordinary limits of accuracy, and for this reason the volume of precipitate can be neglected in ordinary work. Tables III and IV show the results obtained with the method.

<sup>1</sup> E. Alefeld, *Z. anal. Chem.*, **48**, 79.



TABLE III

Number and description.	(1) Sample of commercial milk	(2) Sample (1) plus 0.1000 grams NaCl per 100 cc.	(3) Sample (1) plus 0.2000 grams NaCl per 100 cc.	(4) Sample (1) plus 0.3000 grams NaCl per 100 cc.
N. Y. Bd. of H. lactometer reading at 60° F.	112	114	116	118
Corresponding specific gravity.	1.0325	1.0331	1.0336	1.0342
Fat by Babcock test.	4.3	4.3	4.3	4.3
Total solids	13.23	13.36	13.43	13.53
Ash	0.753	0.848	0.949	1.037
Sodium chloride by direct ashing	Per cent. by weight... 0.163	0.258	0.347	0.442
Grams per 100 cc.	0.168	0.266	0.359	0.457
Sodium chloride by ashing with sodium carbonate.	Per cent. by weight... 0.169	0.270	0.361	0.453
Grams per 100 cc.	0.175	0.279	0.373	0.469
Sodium chloride by author's method.	Per cent. by weight... 0.171	0.272	0.366	A. 0.466, B. 0.464
To volume of 100 cc.	0.177	0.281	0.378	Average 0.465, A. 0.482, B. 0.480
Sodium chloride by author's method.	Per cent. by weight... 0.169	0.263	0.363	Average 0.431, 0.458
To volume of 200 cc.	0.175	A. 0.271, B. 0.273	A. 0.378, B. 0.372	A. 0.475, B. 0.472
Added sodium chloride found	By direct ashing... 0.098	Average 0.272	Average 0.375	Average 0.474.
Grams per 100 cc.	By ashing with sodium carbonate... 0.104	0.097	0.191	0.289
	By author's method... 0.104		0.198	0.294
	To volume of 200 cc.		0.200	0.299

TABLE IV.

Number	Lactometer reading	Corresponding specific gravity	Fat by Babcock test	Total solids	Sodium chloride by ashing with sodium carbonate		Sodium chloride by author's method.	
					Per cent. by weight	Grams per 100 cc.	Per cent. by weight	Grams per 100 cc.
45768	106	1.0307	3.6	11.83	a. 0.204	0.210	a. 0.197	a. 0.203
45769	110	1.0319	3.7	12.23	b. 0.201	0.207	b. 0.197	b. 0.203
45770	108	1.0313	3.7	12.09	0.166	0.171	0.164	0.169
45771	111	1.0322	3.9	12.54	0.177	0.183	0.180	0.186
45772	108	1.0313	3.6	11.97	0.187	0.193	0.187	0.193
45773	110	1.0319	4.2	12.83	0.221	0.228	0.229	0.236
45774	107	1.0310	4.1	12.50	a. 0.185	a. 0.191		
45775	111	1.0322	3.7	12.30	b. 0.185	b. 0.191	0.177	0.183
45776	110	1.0319	3.3	11.78	0.177	0.183	0.182	0.188
45777	112	1.0325	3.7	12.37	0.170	0.175	0.168	0.173
45778	108	1.0313	3.2	11.52	a. 0.207	a. 0.214		
45779	113	1.0328	3.6	12.32	b. 0.201	b. 0.207	0.200	0.206
45780	111	1.0322	3.9	12.54	0.240	0.248	0.241	0.249
45781	109	1.0316	3.7	12.16	0.200	0.206	0.202	0.208
45782	110	1.0319	3.6	12.11	0.185	0.191	0.182	0.188
45783	113	1.0328	3.5	12.20	0.177	0.183	0.182	0.188
45784	114	1.0331	3.3	12.11	0.186	0.192	0.182	0.188
45785	106	1.0307	3.5	11.71	0.177	0.183	0.172	0.178
45786	113	1.0328	4.0	12.80	0.159	0.164	0.163	0.168
45787	111	1.0322	3.3	11.94	0.174	0.180	0.168	0.174
					0.178	0.184	0.182	0.188

From the results in Table III, it will be seen that the figures by ashing with sodium carbonate and the author's method show reasonably close agreement, but that by direct ashing quite a loss of chlorine occurs. It is interesting to note that the addition of 0.1000 gram of sodium chloride to 100 cc. of milk causes an increase of 2° in the lactometer reading or 0.0006 in the specific gravity. In judging whether a sample of milk contains added sodium chloride the ratio of total ash to sodium chloride can be depended upon to show such addition. In this connection, the figures given in Table V, taken from Table III, show the effect on this ratio when sodium chloride has been added.

From the composition of milk ash, as given by Richmond,<sup>2</sup> the ratio of ash to sodium chloride is

4.33. Blyth<sup>1</sup> gives the ratio 3.74. According to Fleischmann and Schrott<sup>3</sup> the ratio is 4.15. König<sup>3</sup> gives the ratio 4.52. Through the courtesy of Dr. Deghuae, of the Lederle laboratories, it is hoped to extend the study of this ratio.

TABLE V

Number and description.	Ash, per cent.	Sodium chloride, per cent. by weight.	Ratio of ash to sodium chloride.
(1) Sample of commercial milk.	0.755	0.169	4.47
(2) Sample (1) plus 0.1000 gram NaCl per 100 cc.	0.848	0.263	3.23
(3) Sample (1) plus 0.2000 gram NaCl per 100 cc.	0.949	0.363	2.61
(4) Sample (1) plus 0.3000 gram NaCl per 100 cc.	1.037	0.458	2.26

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF MISSOURI.]

## PHOSPHORUS IN FLESH.

(SECOND PAPER).<sup>4</sup>

By P. F. TROWBRIDGE AND LOUISE STANLEY

Received March 11, 1910.

Hart and Andrews<sup>5</sup> were among the first to show that the phosphorus in foods was present to a considerable extent in the organic form. They claimed that in precipitating the phosphorus from the water solutions in the usual way with the ordinary acid molybdate, a sufficient quantity of acid was present to cause a splitting of the soluble organic phosphorus and a precipitation of it along with the inorganic forms. They proposed to remedy this defect by precipitating with neutral molybdate in the presence of the smallest necessary amount of nitric acid. In their method, as finally worked out, they used 10 grams of ammonium nitrate and 2 cc. of nitric acid. Under these conditions only a very small amount of the

<sup>1</sup> "Foods," 1903, p. 201.

<sup>2</sup> See Wiley's "Agric. Anal.," Vol. III, p. 467.

<sup>3</sup> Chem. Weekl. u. Genussm., **11**, 227.

<sup>4</sup> This Journal, **1**, 675 (1909).

<sup>5</sup> Am. Chem. J. **30**, 470 (1903).

<sup>1</sup> N. Y. Bd. of H. lact

<sup>2</sup> "Dairy Chem.," p. 32.

molybdate precipitate of inorganic phosphorus was obtained, and upon this they base their assertion that practically all the water-soluble phosphorus in vegetable feeding-stuffs is in the organic form.

As a test of this method a solution of inorganic phosphorus was made up, equal definite amounts were taken and the above method of precipitation tried in comparison with the usual methods. The results are noted in the table below. It is quite evident that the Hart and Andrews method fails to precipitate all the phosphorus even when it is present in the inorganic form. If this be true with simple water solution of inorganic salt, it is not surprising that under the retarding conditions usually present in the water extracts of flesh one should fail to get a complete precipitation with the neutral molybdate.

PRECIPITATION OF PHOSPHORUS BY NEUTRAL AMMONIUM MOLYBDATE

Molybdate used	Acid added		Yield of P as $Mg_2P_2O_7$ gram
	Ammonium nitrate	$HNO_3$ (sp. gr. 1.42)	
25 cc of usual acid	10	Acidified	0.076
25 cc of neutral	10	2 cc	0.0461
25 " " " "	10	3	0.0618
25 " " " "	10	4	0.0634
25 " " " "	15	2	0.0444
25 " " " "	20	2	0.0481

Emmett and Grindley<sup>1</sup> studied the method with a view to its application in determining the organic phosphorus in cold water extracts of flesh. The presence of the soluble protein made it impossible to apply the method without first removing the coagulable protein. This they did by evaporating the solutions to a small volume, and filtering out the coagulated proteins. The method of Hart and Andrews gave good results with the filtrate and they found that as high as 20 cc. of nitric acid could be used without perceptibly affecting the results.

The work of Emmett and Grindley seemed to show that nearly all the soluble phosphorus in flesh was present in the inorganic form. During the years 1907 and 1908 at the Missouri Experiment Station we used the above method in determining the inorganic phosphorus in the cold water extracts of flesh and our results confirmed the belief that in flesh the soluble phosphorus was almost entirely present in the inorganic form. To illustrate we show in the table below the results of determinations upon cold water extract of flesh for total and for inorganic phosphorus. These results indicate quite clearly that after the treatment to remove the coagulated protein the phosphorus is present in the inorganic form.

Siegfried and Siegwald<sup>2</sup> separated organic from inorganic phosphorus in meat extract by the precipitation of the inorganic phosphorus with barium chloride in solution alkaline with ammonia. They found that this gave a sharp separation and by determining the phosphorus either in the filtrate or in the

precipitate could get at either the organic or inorganic phosphorus.

Sample	Per cent. total phosphorus	Per cent. inorganic phosphorus
8270 Lean and fat of beef, composite	$\bar{g}$ 0.1225 $h$ 1.051 $i$ 0.1180	$\bar{g}$ 0.1205 $h$ 0.1139 $i$ 0.1144
Average	0.1203	0.1163
8271 Lean beef	$\bar{g}$ 0.1609 $h$ 0.1620 $i$ 0.1615	$\bar{g}$ 0.1615 $h$ 0.1629 $i$ 0.1668
Average	0.1615	0.1637
8272 Sample of beef fat	$\bar{g}$ 0.0312 $h$ 0.0351 $i$ 0.0329	$\bar{g}$ 0.0388 $h$ 0.0462 $i$ 0.0296
Average	0.0330	0.0382

A comparison of these two methods gave such strikingly different results that we were led to investigate more thoroughly.

In the preparation of the cold water extracts of the raw meats or of the cooked meats the following method was followed:

120 grams of finely ground lean meat (180 grams if sample was very fat) were distributed in twenty 150-cc. beakers. Each portion was wetted with two or three cc. of neutral recently boiled distilled water and mixed to a paste and then more water added to make a total of 50 cc. The water was allowed to stand on the sample for about half an hour with frequent stirring. It was then transferred to a filter and the solution allowed to drain completely. The residue was returned to the beaker and was thoroughly mixed with 25 cc. of the distilled water and again filtered. This operation was repeated with each of the 20 portions of the sample, until a total of 250 cc. of water had been used. Each residue on the filters was then washed twice with 10 cc. of water. The total filtrate was then measured into a large bottle and with rinsings from the 20 flask made up to exactly 6 liters mixed thoroughly without too much aeration and filtered through dry filters. From the filtrate aliquots for the analyses were taken. For total phosphorus 500-cc. portions were evaporated to small volume in beakers on the steam bath, then with fifteen cubic centimeters of sulphuric acid transferred to nitrogen flasks and digested as for nitrogen, using mercury and potassium sulphate. The contents of the flask were transferred to beakers, and the phosphorus estimated in the usual manner as magnesium pyrophosphate after first precipitation with acid ammonium molybdate and re-solution in ammonia.

Other 500-cc. portions of the filtrate were coagulated by evaporation to a small volume filtered and the coagulum thoroughly washed with hot water. The filtrate and washings were then made alkaline with ammonia and the inorganic phosphorus precipitated by the addition of barium chloride. The organic phosphorus was estimated in an aliquot of the filtrates as described above for total phosphorus.

<sup>1</sup> Jour. Am. Chem. Soc., 28, 25 (1906).

<sup>2</sup> Zeit. Nahr. u. Genussm., 70, 521.

Still other 500-cc. portions were treated with ammonia and barium chloride (without previous heating) for the precipitation of the inorganic phosphorus and the organic phosphorus determined in an aliquot of the filtrate as described above for total phosphorus.

A sample of raw beef (No. 810292) showed 7.15 per cent. of the total soluble phosphorus to be organic when the solution was first coagulated and 85.52 per cent. of the total soluble phosphorus to be organic when the inorganic phosphorus was removed by the ammonia and barium chloride without heating.

In another sample of raw beef (No. 810295) only 0.86 per cent. of the soluble phosphorus is organic after coagulating by heat and 86.30 per cent. by removing the inorganic phosphorus with ammonia and barium chloride without heating. A portion of this sample was cooked as a beef loaf which was reground, thoroughly mixed and a water extract prepared as for raw meats. In this case 7.4 per cent. of the soluble phosphorus is organic after coagulating by heat and 17.6 by removal of the inorganic phosphorus with barium chloride and ammonia.

In a third sample of raw beef (811x) 6.3 per cent. of the total soluble phosphorus is organic after coagulating by heat and 57.4 per cent. by use of barium chloride and ammonia without heating. A portion of this sample was also cooked as a beef loaf and a water extract prepared as above. Only a trace of organic phosphorus was found after coagulating and 16.5 per cent. of the total soluble phosphorus was organic after separated by barium chloride and ammonia without heating. The following table summarizes the results given above.

From this it would seem that the long-continued heating has either caused a splitting of the simple

organic phosphorus compounds and a precipitation of them in the inorganic forms, or else on the other hand the presence of the protein seems to hold back some of the precipitate of barium phosphate.

COMPARISON OF ORGANIC PHOSPHORUS FROM WATER EXTRACTS OF MEAT BEFORE COAGULATING AND AFTER COAGULATING

Lab. No.	Sample	Total phosphorus in extract, per cent.	Organic phosphorus without coagulating, per cent.	Organic phosphorus after coagulating, per cent.	Organic phosphorus in extract without coagulating, per cent.	Organic phosphorus after coagulating, per cent.
810292a	Raw chuck loaf	0.163	0.141	0.017	86.53	10.43
810292b	Raw chuck loaf	0.164	0.138	0.007	84.146	4.27
810295	Shank loaf raw	0.162	0.140	0.001	86.420	0.62
810295	Shank loaf cooked	0.151	0.026	0.011	17.219	7.28
811x	Chuck loaf raw	0.168	0.096	0.011	57.143	6.35
811x	Chuck loaf cooked	0.152	0.025	Trace	16.447	Trace

In another series of experiments the total phosphorus and organic phosphorus were determined in water extract of samples of raw meat, a portion of the same meat was cooked as beef loaf to a definite temperature and a roast of the same cut was taken from the opposite side of the animal. The total phosphorus was determined in the usual way after Kjeldahl digestion of 500 cc. aliquots of the water extract (representing 10 gr. of original meat sample). For the organic phosphorus 600 cc. (12 grs.) were taken to which 10 cc. of barium chloride, 5 cc. of ammonia, and 45 cc. of distilled water were added. This was shaken well, allowed to stand over night and filtered in the morning. 550 cc. of the filtrate (representing 10 grs. of original material) were used for the organic phosphorus. The samples from the raw meats gave very little precipitate and the filtrates were in every case slightly cloudy. The extract from the cooked samples gave a heavy precipitate and in every case the filtrate was clear. The following table gives a summary of the results obtained, being the average of triplicate determinations:

DISTRIBUTION OF THE PHOSPHORUS IN BEEF FLESH.

Lab. Number.	Animal.	Description of sample.	Temperature of cooked meat. <sup>2</sup>	Total phosphorus in meat, Per cent.	Total phosphorus in water extract soluble, Per cent.	Organic phosphorus in water extract, Per cent.	Inorganic phosphorus in water extract, Per cent.	Soluble phosphorus which is organic, Per cent.	Total phosphorus which is soluble, Per cent.
81224-25	504	Round, raw.		0.160	0.145	0.0758	0.0692	52.28	90.625
81245	504	Round loaf.	60° C.	0.192	0.1401	0.0388	0.1013	27.69	72.969
81249	504	Round inside muscle.	68° C.		0.1237	0.0355	0.0882	28.70	
81226-27	504	Loin raw.		0.126	0.0882	0.0520	0.0332	61.03	67.619
81246	504	Loin loaf.	65° C.	0.200	0.1443	0.0331	0.1112	22.96	72.150
81248	504	Loin roast.	60° C.		0.1221	0.0339	0.0882	27.76	
81228-29	504	Rib raw.		0.131	0.0977	0.0692	0.0285	70.83	74.580
81247	504	Rib loaf.	60° C.	0.182	0.1335	0.0319	0.1016	23.87	73.352
81250	504	Rib 11th and 12th standing.	64° C.		0.1386	0.0343	0.1043	24.75	
9168	592	Composite of carcass.		0.174	0.128	0.0333	0.0947	26.02	73.563
91151	592	Composite as loaf.	60° C.		0.1615	0.0253	0.1362	15.67	
91124	48	Round raw.		0.192	0.1513	0.1247	0.0266	82.42	78.802
91152	48	Round loaf.	61.5° C.		0.1643	0.0509	0.1134	30.98	
91155	48	Round inside muscle.	62° C.		0.1426	0.0326	0.1100	22.86	
91126	48	Loin raw.		0.174	0.1365	0.0990	0.0375	72.53	78.448
91153	48	Loin loaf.	60° C.		0.1557	0.0453	0.1104	29.09	
91156	48	Loin roast.	64° C.		0.1481	0.0385	0.1066	26.53	
91128	48	Rib raw.		0.150	0.1217	0.106	0.1111	87.10	81.133
91154	48	Rib loaf.	60° C.		0.1440	0.0407	0.1033	28.26	
91157	48	Rib 11th and 12th standing.	60° C.		0.1275	0.0306	0.0969	24.00	
92152	Jerry	Rib raw.		0.152	0.118	0.1089	0.0091	91.44	77.632
92166	"	Rib loaf.	60° C.		0.1429	0.0337	0.1092	23.58	
92167	"	Rib loaf.	80° C.		0.1468	0.0306	0.1162	20.86	
92168	"	Rib loaf.	98.5° C.		0.1449	0.0162	0.1487	9.82	

<sup>1</sup> In terms of total soluble phosphorus.

<sup>2</sup> The temperature of the cooked meat is that registered by the center of the meat when removed from the oven.



## CONCLUSIONS.

Emmett and Grindley's method does not give high enough results for organic phosphorus in cold water extracts of flesh, as the heat of coagulation has changed nearly all of the organic phosphorus to the inorganic form.

Barium chloride in slightly ammoniacal solution precipitates the inorganic phosphorus from water extracts of flesh and gives a satisfactorily accurate separation of the inorganic from the organic form.

There seems to be a progressive splitting up of the organic phosphorus compounds in beef flesh during the process of cooking so that in well done meats practically all the phosphorus is present in the inorganic form.

A study of the tables shows considerable variation in the relative amounts of soluble and soluble organic phosphorus in different cuts and in different animals. Extremes will be noted in rib of Jerry (a fat show steer) in which 91.44 per cent. of the soluble phosphorus is organic and in composite of 592 (an extremely emaciated steer) where only 26.02 per cent. or the soluble phosphorus is organic. This subject is being investigated further.

COLUMBIA, MO., March 9, 1910.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY  
UNIVERSITY OF MISSOURI]

## THE GLYCOGEN CONTENT OF BEEF FLESH.

(SECOND PAPER.)

By P. F. TROWBRIDGE AND C. K. FRANCIS.

Received February 17, 1910.

In continuing this study<sup>1</sup> the following points were especially considered.

(1) The disappearance or diminution of the glycogen in the flesh of a starving animal.

Smith's "Veterinary Physiology"<sup>2</sup> contains the following: "The glycogen which is stored up in the liver for future use may be made to disappear by starving and working the animal." The same author on p. 227 says: "The muscles of well fed animals contain a considerable quantity of glycogen. Ordinarily it may be stated that the muscles hold as much glycogen as the liver."

(2) The rapidity with which the glycogen disappears after death.

Roehmann,<sup>3</sup> experimenting with dogs, shows that the hydrolysis after death takes place, but not so rapidly but that the major portion can be recovered as glycogen in from one-half to two hours after death. Under certain conditions rigor mortis may take place without loss of glycogen.<sup>4</sup>

(3) The glycogen in horse flesh as compared to that in beef.

Without indicating the method of analysis, Lebbin<sup>1</sup> has reported horse flesh to contain on an average 0.7 per cent. of glycogen, while Pflüger<sup>2</sup> using the alkali method has found from 1.5 to 2.2 per cent.

"Even after nine days' starvation the muscles of horses have shown a glycogen content of from 1 to 2.4 per cent."<sup>3</sup>

Among the results published in the previous paper<sup>4</sup> we desire to recall to the reader the glycogen determinations on the lean meat from three animals. The percentages of glycogen in these have been averaged and reduced to a moisture- and fat-free condition. Other particulars are indicated in the table below.

TABLE I.—GLYCOGEN IN LEAN CLOD MUSCLE.

Lab. No.	Glycogen in sample		Kind of animal.	Condition of animal	Age
	Glycogen calculated in fresh to fat and sample, per cent.	H <sub>2</sub> O free, per cent.			
92103	0.697	3.38	Jersey cow	Lean	6 years.
91103	0.663	2.95	Short-horn steer	Very fat	4 1/2 yrs.
9153	0.416	1.82	Hereford steer	Emaciated (starving)	23 mos.

While the amount of glycogen in the lean flesh of the Jersey cow is more than that found in the fat steer, the fact that the cow was in a thrifty condition should be considered. It may be that age is an important factor, or that the function of the animal in milk production bears some relation to the storage of glycogen. The thin Hereford steer was not starving in the sense that all food was withheld, but for eleven months he was so fed as to make him lose one-half pound each day. His condition was such at the time of slaughtering that he could not walk steadily but could get up of his own accord. Notwithstanding this emaciated condition and the fact that the entire carcass contained no fat which could be separated mechanically, the muscle still showed the presence of glycogen in considerable quantity.

The following table shows the glycogen content of the liver from a fat Jersey cow, about 7 years old and not in milk for 12 months previous to the date of slaughtering. The animal was killed at 10:18 A.M. and the liver received at the laboratory at 11:30 A.M. and the first portion placed in alkali at 12:05. The elapsed time indicates the interval required to remove the organ, grind, weigh and place the sample in the alkali.

TABLE II.—GLYCOGEN IN LIVER OF COW NO. 43.

Lab. No.	Sample.	Glycogen, per cent.	Elapsed time.
91052 x	Liver	2.91	1 hr. 47 min.
91052 y		3.07	1 hr. 51 min.
91052 z		2.83	1 hr. 57 min.

Table III shows the analysis of the liver from another fat Jersey cow, about 9 years old and not in milk for 12 months previous to the date of slaughtering. The animal was killed at 8:10 A.M. and the liver re-

<sup>1</sup> THIS JOURNAL, 2, 21, (1910).

<sup>2</sup> Manual of Veterinary Physiology," F. Smith, 3rd Ed. p. 226.

<sup>3</sup> Roehmann, *Biochemie*, 229, 1908.

<sup>4</sup> *Ibid.*, p. 236.

<sup>1</sup> *Z. Nahr Genussm.*, 7, 747

<sup>2</sup> *Ibid.*

<sup>3</sup> Smith's "Vet. Physl.," p. 227.

<sup>4</sup> *Loc cit*

ceived at the laboratory at 9:45 A.M. and the first portion placed in alkali at 10:14.

TABLE III.—GLYCOGEN IN LIVER OF COW No. 4.

Lab. No.	Sample	Glycogen, per cent.	Elapsed time.
9102 x	Liver	3.09	2 hrs. 6 min.
9102 y		3.18	2 hrs. 13 min.
9102 z		3.12	2 hrs. 21 min.

The remaining portion of the above sample was placed in cold storage for one week, the temperature remaining about 6.5° C. Triplicate determinations were then made which gave results indicated in Table IV.

TABLE IV.—GLYCOGEN IN LIVER OF COW No. 4 AFTER ONE WEEK.

Lab. No.	Sample	Glycogen, per cent.	Elapsed time.	Condition of sample.
9102 xx	Liver	2.78	1 week	Fresh
9102 yy		2.66	1 week	Fresh
9102 zz		2.81	1 week	Fresh

The remaining portion of the sample was returned to the cold storage and the same temperature maintained for another week. When removed on the 14th day the sample appeared to be in about the same condition, so it was decided to expose it in a sealed bottle to atmospheric temperature before analyzing. The results of the analysis after that time are shown in Table V.

TABLE V.—GLYCOGEN IN LIVER OF COW No. 4 AFTER 15 DAYS.

Lab. No.	Sample	Glycogen, per cent.	Elapsed time.	Condition of sample.
9102 xxx	Liver	2.06	15 days	Slightly spoiled.
9102 yyy		2.32		
9102 zzz		2.36		

Portion 9102 xxx was intentionally removed from the bottle without its being mixed with the remainder of the sample, as it showed evidence of decomposition, being covered with mold. The results were somewhat higher than we expected after the sample had been exposed for eighteen hours to the temperature of the air. Upon obtaining the records from the local weather bureau a rather interesting fact became apparent: the average temperature for the eighteen hours was 6.6° C. As we have previously demonstrated that low temperatures check the hydrolysis of glycogen, no great change could be expected in this instance.

*Experiments with Horse Flesh.*—A horse thin but not in starving condition, about twenty years old, was killed and a portion of lean muscle from low in the neck used for the glycogen determination.

In the tables below the elapsed time indicates the

TABLE VI.—GLYCOGEN IN HORSE FLESH.

Lab. No.	Glycogen, per cent.	Elapsed time.	Temperature.	Condition of sample.
91190 x	0.183	30 min.	20-25	Fresh
91190 y	0.122	37 "		
91190 z	0.133	41 "		
91190 xx	0.066	22 hrs.	23	Fresh
91190 yy	0.077	22 "		
91190 xxx	0.014	3 days	20	Slightly decomposed.
91190 yyy	0.015	3 "		
91190 zzz	0.010	3 "		

time passed after the death of the horse before the sample was placed in alkali. The temperatures mentioned are those to which the sample was subjected for the period given previous to the analysis.

The above results show that horse flesh is subject to an enzymatic hydrolysis similar to that of beef. At the end of 22 hours the loss of glycogen was equal to 51.4 per cent. and at the end of 3 days to 91.1 per cent.

#### SUMMARY AND CONCLUSIONS.

1. The glycogen content of beef muscle and beef liver varies from 0.1 to 0.7 and 0.2 to 3.8 per cent. respectively.
2. Starvation or extreme debility does not cause entire removal of glycogen from the muscle or liver.
3. The glycogen of beef liver and muscle slowly decreases, but does not entirely disappear, when kept at a temperature of 6.5° C. for over two weeks. Glycogen may be present even when liver has become unfit for food.
4. Horse flesh is subject to an enzymatic hydrolysis of the glycogen similar to that of beef. The glycogen decreases slowly when the sample is exposed to temperatures of about 20-25°.
5. The glycogen content cannot be said to offer an absolute or even approximate basis for distinguishing beef from horse flesh.

COLUMBIA, MO., Feb., 1910.

## ADDRESSES.

### VEGETABLE TANNING MATERIALS.<sup>1</sup>

By JOHN H. YOCUM, Ladew and Yocum Tanneries, Newark, N. J.

When in the time that our tanners had the virgin forest to depend upon, hemlock and oak bark were the only vegetable tanning materials in use in this country, and they yet remain the source of greatest supply of tannin.

The yearly cut of hemlock bark is between 800,000 and 900,000 tons, and oak bark from 300,000-400,000 tons. The peel of hemlock has decreased about one-third in the last ten years, while the peel of oak bark has remained nearly stationary.

Because of increased production of leather during this period and because of the decrease in the peel of hemlock bark, it has become necessary to reach other sources of tannin supply.

The first development to meet these conditions was the making of chestnut wood extract, which has now reached a very important stage, from 450,000-500,000 bbls. being produced yearly. In addition chestnut wood is being used at many southern tanneries directly in the leaches. Tanners have found that the liquors obtained by this method are insufficient in strength for their purposes, so some of them have added evaporating plants to their leach houses to concentrate their liquors to a sufficient strength for their use.

A barrel of chestnut extract is practically equal to a ton or cord of either oak or hemlock bark, and while the yield from various extract factories differ, generally a cord of wood (128 cubic feet) yields a barrel of the 25 per cent. tannin chestnut extract.

Quebracho extract is made from quebracho wood, a product

<sup>1</sup> Address before New York Section American Chemical Society Symposium on Leather.

of the River Platte Valley in South America. This wood contains from 18-24 per cent. tannin.

The solid quebracho extract contains about 65 per cent. tannin and is sold on this basis. The yield of extract is generally one ton of solid extract from about three and one-half tons of the wood. One ton of the solid extract is considered equivalent to nine tons of oak or hemlock bark.

There are now being imported about 60,000 tons of this solid extract or its equivalent in wood; as there are two factories manufacturing liquid quebracho in this country, the equivalency of this quantity of quebracho is 540,000 tons of oak or hemlock bark.

The tariff on this product was formerly  $\frac{1}{2}$  cent per pound, but it has been raised to  $\frac{3}{4}$  cent per pound in the new tariff bill.

Mangrove bark and mangrove extract are also imported in quantity. Mangrove bark grows on the low shores of salt waters everywhere in the tropics. Along the Gulf of Mexico, mangrove averages, when properly cured, about 30 per cent. tannin; that from the East coast of Africa about 40 per cent. tannin. East Indian and Borneo, between the two; this product enters free of duty, so that no accurate data is obtainable as to the quantity imported, but this no doubt is more than 20,000 tons annually, equivalent to more than 60,000 tons of oak or hemlock bark.

In the East Indies are two factories making solid extract from this bark, which comes upon our market as mangrove cutch; the quantity being brought in is not large now on account of the duty of 7/8 cents per pound, which the new tariff has placed on this product. It formerly came in free.

Myrabolans are the fruit of an Indian tree, the harvest ranging from 30,000-45,000 tons per year. The United States is taking from one-third to one-half the production. Myrabolans contain about 30 per cent. tannin. What is now being used in the tanning trade in this country will represent at least 45,000 tons of oak or hemlock bark. It comes in free of duty.

Valonia, the cup of an acorn obtained in Asia Minor and Greece, is being imported in quantity; it contains about 40 per cent. tannin. The harvest is from 50,000-60,000 tons per year. What is being brought into this country is equivalent to about 40,000 tons of bark per year. It comes in free of duty.

Divi-divi, wattle bark, etc., do not come into this country in any quantity.

Palmetto extract and canaigre are not produced in sufficient quantities to be commercially considered. Sumac and gambier are imported in large quantities, but do not go into the same trade that uses our native barks and cannot be compared with them.

From the estimates given of what the various tanning materials in use here are equivalent to in bark, it is seen that in total 2,300,000 tons are represented, about one-third being imported materials. At a fair valuation, these materials cost the tanner about \$23,000,000, the importations being about \$7,000,000 per year.

From a chemical view-point, tannins are divided into pyrogallol tannins, such as those from chestnut wood, myrabolans and valonia; and catechol tannins, such as from quebracho, hemlock, mangrove and oak bark. But from the tanners' view-point, the color and characteristics of the leather made from these various materials is of more importance.

Arranging these materials as to their color, that is from a light yellow to a dark red, we have sumac, myrabolans, valonia, bleached quebracho, oak bark, natural quebracho, chestnut, West Indian mangrove, hemlock, and East African mangrove.

It is important to a tanner of oak so far as color is concerned, that if he uses chestnut, to also use quebracho, so that a duplication of the oak color be obtained. There are many combinations that can be arranged from these materials to duplicate the

oak, hemlock or union colors so long established as standards in the sole leather trade.

The color of the leather produced is not the only characteristic which the tanner has to consider in the use of tanning materials; some wish hard leathers, some soft. It is well established that sumac is not suitable for hard leather; it is used on sheep and other soft leather exclusively. Myrabolans are considered a soft tannage. Valonia and chestnut are considered hard tannages. Oak, hemlock, mangrove and quebracho are used on both hard and soft tannages. There seems good reason to believe that by proper manipulation soft leathers can be obtained from any of these materials.

Palmetto extract which often contains as much as 12 per cent. of ash from salts soluble in the extract, the extract containing about 20 per cent. tannin, invariably makes soft leathers when used alone. Sulphited quebracho extracts which contain a large per cent. of ash also make soft leathers, and it is a well-known fact that hemlock liquors treated with common salt will tan sheep skins as soft as does sumac.

From this it is a fair conclusion that salts in tanning solutions have a tendency to soften the resulting leather.

In tanning pickled sheep skins, that is, skins cured in NaCl and  $H_2SO_4$ , unless the tanning solution is salted; that is, treated with NaCl, the skins plump and lose their value, becoming hard and tinny when tanned; that is, NaCl counteracts the action of the  $H_2SO_4$  on skins.

The tanners of the hardest sole leather use  $H_2SO_4$  as a plumping agent, using hemlock, oak, mangrove, valonia, chestnut, myrabolans and quebracho in various mixtures and proportions. It follows that the character of leather as to softness or hardness is more dependent on the relation of plumping acids to soluble non-tannins than it is on the character of the tanning material used.

In using the term soluble non-tannins, I wish to include the effect not only of soluble inorganic salts, but also the similar effect of organic non-tannins natural to the tanning material.

The character of the organic non-tannins vary both as to their ability to furnish plumping acids and non-plumping acids, and likewise as to their depression of plumping acid action on the skin.

It is quite true as a rule that the pyrogallol tannins do not give the hard leathers that the catechol tannins produce, yet this may not of itself be due to the character of the tannin, but may result from the fact that gallic acid and non-plumping acid is usually present in the tanning solutions made from these materials.

The subject is a broad one and needs much investigation, but sumacs and nutgalls of the pyrogallols series show the largest changes into gallic acid and give the softest leather, while valonia of the same series shows small changes into gallic acid and gives a firm leather. On the other hand, chestnut extract contains in its extracted form gallic acid, and not subject to much further changes into this acid, gives a firm leather.

Palmetto is of the catechol series, but gives a soft leather, which as I have noted before may be due to the presence of excessive quantities of inorganic salts, yet all the rest of this series are used for heavy leather tannages.

The nature of the combination of hide with tannin is not fully understood at present, but the tanner has had the experienced knowledge of generations in the use of raw vegetable tanning materials. This knowledge seems to have brought the practical tanner to conclusions, and he has determined in his own mind what raw material he wants to use to produce a certain result.

It lies with the chemist to determine the reactions between the different tannins, non-tannins and their relations to salts and acids before the final decision can be reached as to the



weakness or strength of the rule of thumb methods now followed by the tanner in determining the kind of tanning material to be used by him.

### DYEING LEATHER.<sup>1</sup>

By F. E. ATTEAUX, President, F. E. Atteaux and Co., Boston.

The art of dyeing leather was known to the early Egyptians over three thousand years ago. They produced finely colored leather, samples of which have been found and preserved.

The Chinese and various Oriental tribes also understood the art, and produced highly colored and embossed leather, similar to morocco. They were the first to introduce colored leather in Europe.

After a time the races of Europe began to learn the process of manufacture and coloring leather for their own consumption. As time went on the art of dyeing leather increased. Processes were improved and at the present time the methods employed are radically different from those used only a few years ago.

Formerly vegetable coloring matters were in great demand for dyeing leather, but now these products have been replaced one by one with the artificial dyestuffs, and to-day only a few vegetable colors are used, the most important of which are logwood and fustic.

Of the artificial or so-called aniline dyes, those especially adapted for leather dyeing are the acid, basic, direct and alizarine dyestuffs.

These act differently on different tannages.

**Chrome Tannage.**—The process of dyeing the different kinds of chrome-tanned leather such as calf, sheep, goat and heavy leather, also pig and horse hides are similar and the formula used on one may be applied to all, with good results, the only difference being a slight variation in body or shade due to the nature of the skin and the method of chrome tannage.

Before dyeing, the skins should be thoroughly washed and if necessary cleared with dermiforma or lactic acid; then if desired a bottom of some vegetable coloring or tanning matter may be applied, such as gambier, sumac, quebracho or fustic, but this is not necessary only where basic colors are used, when a tannin mordant or bottom is required.

To obtain best results for sumac or gambier bottom, drum for 20 minutes at 100° F., neutral, with 3-6 per cent. of extract, the amount used depending upon the strength of bottom.

The liquor is then run off and  $\frac{1}{2}$ -1 per cent. tartar emetic is added, dissolved in a sufficient quantity of water, and drummed 15 minutes longer at normal temperature; rinse well before dyeing.

Fustic is applied in the same manner as the sumac with the exception of the tartar emetic bath which may be omitted.

From 1-3 per cent. of the extract may be used. This makes a good bottom for acid, direct or alizarine dyes, but should not be used for basic dyes, as it has but little affinity for them.

On dyeing heavy chrome leather with fustic this process and the fat-liquoring may be combined by first dissolving the fustic and then adding it to the drum together with the fat-liquor and drumming 20-30 minutes.

Alizarine colors can be dyed directly upon chrome leather either with or without a vegetable bottom. They are dyed with the percentage of color required to obtain shade for 20 minutes at 120° F. in neutral or slightly acid bath. If acid is used the best results are obtained by using 1-2 per cent. acetic acid.

These colors are used mostly on calf and heavy leather.

Alizarine orange R and alizarine yellow G are the most extensively used of these colors. By shading with logwood or alizarine blue a variety of tans and browns can be obtained.

Direct colors dye leather in a neutral or slightly alkaline bath.

<sup>1</sup> Address before New York Section, American Chemical Society, Symposium on Leather.

They are drummed for 20 minutes at 120-130° F. From 1-3 per cent. of color should be used, the quantity depending upon the shade desired. If necessary  $\frac{1}{4}$ - $\frac{1}{2}$  per cent. of sal soda may be added to drum and this will insure the leather against acidity.

Wash leather well after dyeing.

By using 4 per cent. soluble oil, or some other light fat-liquor in the dye solution it is possible to fat-liquor and dye in the same bath.

Any of the direct colors can be used and by the combination of colors a great variety of shades can be produced.

Direct colors are now used extensively in combination with logwood for producing black on calf and cow hides.

**Basic colors** are dyed similar to the *direct* colors only in a neutral bath at 110° F.; by adding  $\frac{1}{4}$  per cent. bichromate of potash to drum after dyeing and running 15 minutes longer it will produce darker shades. These colors are used on all classes of chrome-tanned leather.

Phosphine produces various shades of tan ranging from a light yellow to the brown.

Bismarck- and chocolate-browns, malachite-green, fuchsin, auramine, methyl violet and methylene blue are colors of this class. They are fast to nearly all fat-liquors excepting a strongly alkaline fat-liquor which is liable to strip the color.

**Acid colors** are dyed by using  $\frac{1}{4}$ - $\frac{1}{2}$  per cent. sulphuric acid with the dyestuff. This is not necessary with all acid colors, some of which will dye neutral but many of them will not color the leather unless acid is used.

Acetic or formic acid may be used in place of sulphuric.

Leather can be drummed in a weak acid solution and color added in small quantities until the desired shade is obtained.

With these colors it is best to use a neutral or light fat-liquor, or fat-liquor before dyeing. Golden and coffee-browns are combinations of dye belonging to this class.

Colors very fast to light and fat-liquor can be obtained by dyeing the leather with 2 per cent. of dye in a drum for 20 minutes at 120° F. in a neutral bath.

The leather is then washed and run through a cold bath, composed of  $2\frac{1}{2}$  per cent. nitrite of soda and 5 per cent. hydrochloric acid for 15 minutes. It is then washed and put through developing bath of 1 per cent. of phenylamine, diamine, meta-toluene diamine or some other developer for 15 minutes. The bath should be kept cold because resulting colors are apt to be dull or rusty if temperature of bath is too high.

The leather is then fat-liquored, dyed and finished.

Primuline, boma black BH and developed brown R can be dyed by the above formula, good bright colors resulting.

Sulphur colors can also be dyed on leather by first dissolving the dyestuff in as little sodium sulphide as possible and adding it to the drum with 5 per cent. salt and drumming for 20 minutes at 110° F.

**India Tan.**—Before dyeing India goat or sheep skins it is best to clear them with  $\frac{1}{2}$ -1 per cent. tartar emetic or 1-2 per cent. lactic acid, or if necessary re-tan with sumac and then wash thoroughly.

Basic and acid colors are the only class of dyestuffs used upon India skins with satisfactory results.

*Direct* and *alizarine* colors will not dye to advantage and it is considered a waste of material and time to use them.

**Basic colors** dye India-tanned leather very easily as the tannage acts as a mordant, and readily takes up the dye. They produce very bright colors, and are dyed by drumming 120° F. in a neutral bath for 20 minutes. 2 per cent. of the dyestuff produces a full shade.

If an excess of color is used bronzing results, but this may be overcome to a certain extent by using a small percentage of acetic acid with the color.

To dye with acid colors, the skins after being cleared are dyed as follows:

For 1 per cent. color use 0.25 per cent. sulphuric acid, the ratio varying with the amount of color used; they are dyed similar to the basic colors with the exception of the addition of acid; the skins which have been previously treated with sumac and sulphuric acid do not require the addition of acid with the color, as the acid retained in the skins is sufficient to drive on the color.

*Acid* colors are much faster to light than basic colors and produce bright shades.

Leather red 3B, tartrazine, orange A conc., induline and acid green are all extensively used.

*Vegetable Tan.*—Acid and basic colors can both be used upon sumac, gambier, quebracho and other tannages of this class. They are dyed in the same manner as India-tanned skins.

The various combination tannages are also colored in a like manner. If a basic dye will not color with good results the leather should be drummed with sumac and afterwards treated with tartar emetic. The color will then go on properly.

Bark-tanned sheep leather, hemlock splits, etc., are dyed very easily with acid colors and sulphuric acid. If basic colors are desired the leather should be treated with sumac before dyeing. For clearing bark-tanned skins  $\frac{1}{2}$ -1 per cent. borax, and the same quantity of Wyandotte tanners' soda gives good results, but if light shades are desired after clearing the skin with borax or Wyandotte tanners' soda then give them sumac and run for a few minutes in a solution of sulphuric acid of 1 per cent. of the weight of stock. Leather will be much lighter in color.

$\frac{1}{5}$ -2 per cent. tin crystals can be used with sumac to good advantage.

*Heavy oak* or hemlock sole and belting leather are colored by brushing on solution of dyestuff, made up as follows:

$\frac{1}{2}$ -2 oz. of color are dissolved in a gallon of water; acetic acid or methyl alcohol renders the color soluble.

Gum tragacanth and caseine can be used as thickeners. Both acid and basic colors can be used with the gum tragacanth but only acid colors with the caseine, as the alkali used to cut the caseine, will precipitate a basic color. For this reason basic colors cannot be used in any finish or seasoning containing alkali.

*Potassium titanium oxalate* will produce a yellow shade similar to fustic upon any vegetable-tanned leather; it not only acts as a mordant but gives a good yellow bottom for the color. It does not work on chrome leather unless the leather has been previously treated with vegetable tanning material. It is dyed by drumming  $\frac{1}{5}$ -2 per cent. of the compound in a neutral bath at 100° F. for 20 minutes; by using from  $\frac{1}{5}$ -1 per cent. chrome with potassium titanium oxalate various shades of tan and light browns can be obtained depending upon the amount of chrome used.

*Basic colors* can also be used in combination with potassium titanium oxalate.

*Alum* leather is dyed both in a drum and by brushing on color.

Methylene blue and roseine produce delicate tints of blue and pink which are used for fancy leathers. All the basic colors give fine tints and acid colors can also be used on this class of leather.

Chrome, alum and vegetable ooze leathers are dyed with some class of colors previously given under the head of tannages to which they belong and are dyed in the same manner.

For a *black ooze*, the leather is first drummed with a yellow shade Bismarck or potassium titanium oxalate. A direct yellow-brown can be used on chrome ooze; then the leather is drummed with 2-4 per cent. logwood crystals for 30 minutes.  $\frac{1}{5}$  per cent. alkali being added to force on the color.

A striker of acetate of iron or burnt copperas and copper sulphate is then used. It is next fat-liquored and then dyed with  $\frac{1}{5}$ -1 per cent. of neutral or leather black; drummed for  $\frac{1}{2}$  hour at 120° F. and fat-liquored again and then finished.

The amount of aniline color and logwood crystals used depends largely upon the tannage and shade of black desired.

*Nigrosines* are generally classed as basic colors, but they belong to a series of colors known as ingrain colors. They are extensively used in seasonings and finishes for blacks. They can be dyed on chrome leather, either in a neutral or acid bath, but do not give good results when dyed on vegetable tannages.

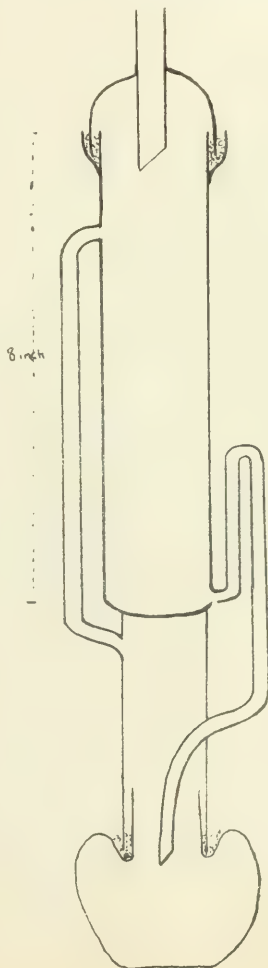
A fine blue-black shade is obtained on the flesh side of the leather by using a little nigrosine in with the logwood when dyeing.

A small percentage of nigrosine brushed on alum ooze leather gives light shades of gray and slate.

## NOTES AND CORRESPONDENCE.

### A MODIFIED SOXHLET APPARATUS.

In order to use as fully as possible the heat from an electric stove for ether extraction a battery condenser was found convenient as it occupied less space than separate glass condensers.



A cheap but efficient condenser was made from a piece of ordinary galvanized iron water pipe into whose ends wooden plugs were inserted through which passed water inlet and outlet tubes and also the block-tin tubes in which the ether was condensed. The water jacket was about 36 inches long. The end plugs were made water-tight by pouring upon their inner surfaces a thick layer of tar. The bottom layer was poured in from the top and the top layer through a hole in the side which was subsequently soldered. The use of such a condenser prevents the employment of ground-joints between condenser and Soxhlet as they are not sufficiently flexible. Knorr's modification was therefore further modified by adding to it a second mercury seal at the upper end. The drawing explains the arrangement. The condenser end was made of glass having the same diameter as the block-tin tubes of the condenser and the junction was effected by first winding on the outside a light cotton soaked in gelatine acetic acid and then covering this while moist with a piece of heavy rubber tube. The rubber tube does not show signs of damage from the ether after several months of use.

V. E. HENDERSON.

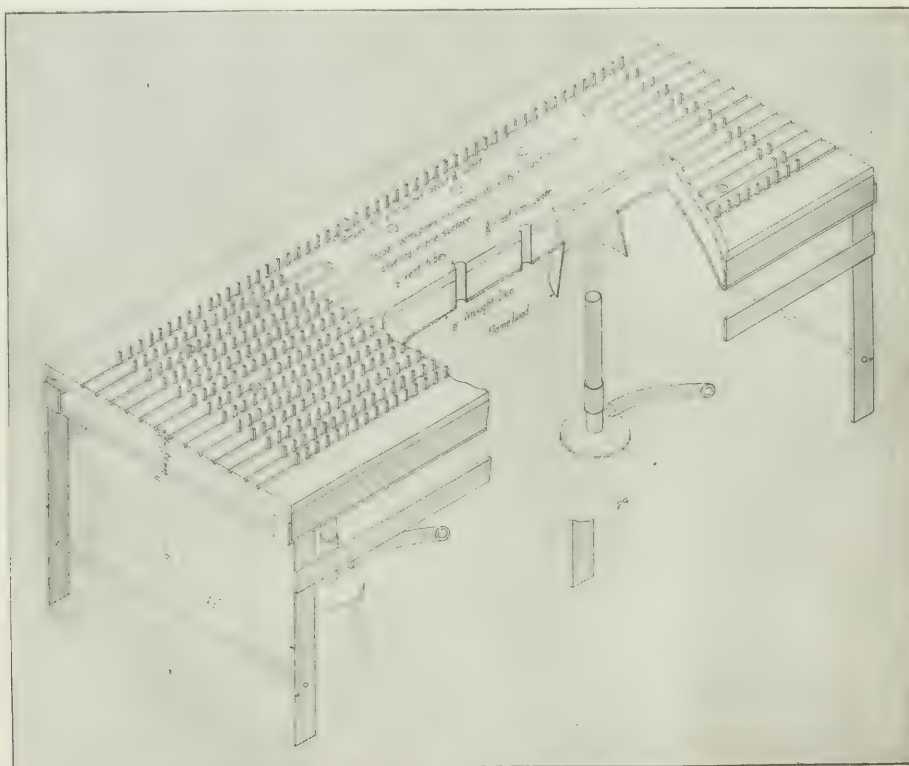
THE PHARMACEUTICAL LABORATORY  
THE UNIVERSITY OF TORONTO.

### AN IMPROVED OVEN FOR HIGH TEMPERATURES.

In the course of some experimental work on methods of

in order to obtain a temperature of  $250^{\circ}\text{C}$ . the copper bottom had to be heated to redness. After a week's use this bottom burned through, hence it became necessary to make some changes in the form of oven.

The old copper bottom was cut away, leaving an inch around the edges and the oven then placed on a separate heating base, the construction of which is shown in the accompanying sketch. This base consists of two iron plates the size of the oven, and one one-fourth inch apart, attached at the sides and open at the ends and connected by a number of one-half inch tight-fitting brass tubes. The upper plate is of three-eighths inch cast iron, the lower is of sheet iron and is used to prevent reflection of heat to the bench. The brass tubes allow the circulation of fresh hot air through the oven. The flame of the burners is applied to the bottom of the cast-iron plate through three-inch holes in the lower plate protected from drafts by circular hoods. Parallel grooves are cut in the upper surface of the cast-iron plate, and copper "porcupines" such as are sometimes used in air-cooled gasoline engine cylinders are expanded into them. The copper porcupines increase the radiation of heat and present a large heating surface to the air currents in the oven. The increased efficiency is so great that a temperature of  $250^{\circ}\text{C}$ . can be maintained without heating the base to redness. The oven has been in daily use for several months and shows no ill effects beyond a slight scaling of the porcupines. These can be renewed when necessary at comparatively slight expense. The oven



asphalt analysis, it became necessary to have an oven temperature of  $250^{\circ}\text{C}$ . for several days at a time. The oven in use at that time was a new single wall, single bottom, copper oven.

base was made according to our plans by the Hamblet Machine Company, Lawrence, Mass.

H. W. CLARK,  
GEORGE O. ADAMS.



## LENGTH OF A TECHNICAL PAPER.

*Editor Journal of Industrial and Engineering Chemistry.*

DEAR SIR:

In the April issue of *THIS JOURNAL*, on page 157, is a note by J. W. Turrentine on the "Length of a Technical Paper."

I wish to endorse all that he says therein. There is often too much abbreviation. The technical paper is written for the eyes and use of some one interested practically in the subject, and too much detail can hardly be given. It is too often assumed that well-trained chemists or men of standing are capable of reading between the lines and supplying the details. They may be capable with the hints given of working the process successfully after they have experimented with it and found what was lacking in the article. For instance the methods for crude glycerine analysis might be boiled down to: weigh out 1.5 grams crude glycerine into a 100 cc. flask, precipitate chlorine and act on reducing matters with silver carbonate, subsequently precipitating organic matters with basic acetate of lead. Make up to mark, filter off an aliquot, rejecting the first portions, take 25 cc. in a 250 cc. flask and add about 42.5 cc. of the bichromate solution and 15 cc. of strong sulphuric acid, etc. There are several very essential details left out of the above for a convenient and correct determination of the glycerol, but to the reviewer, who may not be acquainted with or interested in glycerine, the above appears all that is essential for a trained chemist to have. Give us the details in any articles printed in *THIS JOURNAL* and let the Abstract Journal and Journals on Popular Science or Chemistry handle the articles pruned down to Hints for the Imagination.

Yours truly,

WILSON H. LOW.

NEW YORK, March 17, 1910.

*Chandler Testimonial.* DEAR SIR:

After a very long period, almost a lifetime, of the most useful activity as head of the Department of Chemistry and Dean of the School of Mines of Columbia University, Dr. Charles F. Chandler will retire from duties at the end of the coming term, to be appointed Professor Emeritus of Chemistry. We all know the great service rendered by this distinguished man to our science and to the industries of our country, and it is difficult to convey in words the gratitude which so many of us owe to him who has always been ready to give his advice and to lend his assistance in practical ways.

To commemorate this important epoch in the life of our esteemed friend, the following organizations have taken the initiative in planning for a testimonial to be tendered to Dr. Chandler by the chemists of the United States: The Chemists' Club, The Society of Chemical Industry, The American Chemical Society, The American Electro-Chemical Society, The American Institute of Chemical Engineers, The Verein Deutscher Chemiker.

The form of this testimonial has been arranged as follows:

FIRST: A banquet at the Waldorf-Astoria, on Saturday, April 30th, at 7 P.M. The cost of each dinner ticket will be \$5.00, a sum which, while not sufficient to defray the expenses, will we hope insure a large attendance. Ladies will be admitted to the galleries and light refreshment served them at a nominal charge of \$1.00 per person.

SECOND: The presentation to our honored guest of a bronze bust of himself in heroic size, to be executed by the famous sculptor, Mr. J. Scott Hartley, which bust we expect will finally be presented to the Chandler Museum of Columbia University. A replica of this bust is to be presented to Mrs. Chandler.

THIRD: The Creation of a *Chandler Testimonial Fund* for the purpose of purchasing books for the library of the Chemists' Club.

The committee solicit your subscription for the object set forth, and request you to make your contribution a liberal one, so that a large sum may be collected which will be finally used for the

development of the library of the Chemists' Club, New York, in which, as you know, Dr. Chandler has taken a special interest. This already contains the Perkin Library and is intended to be a reference and circulating library, covering the entire field of theoretical and applied chemistry, which is to be in charge of a salaried librarian, and is to contain duplicate sets, one of which is to be used for circulation among American chemists.

In addition to any personal interest you may take in this testimonial, you are urgently requested to bring the matter of subscribing to this fund, to the notice of any chemical concern with which you are connected, drawing their special attention to the invaluable service which Dr. Chandler has rendered to the industries of this country and to the development of its economic wealth.

Respectfully,

I. F. STONE, Pres. of the Chem. Club,

IRA REMSEN, Pres. of the Soc. of Chem. Ind.,

WILDER D. BANCROFT, Pres. of the Am. Chem. Soc.,

L. H. BAEKELAND, Pres. of the Am. Elec.-Chem. Soc.,

CHARLES F. MCKENNA, Pres. of the Am. Inst. of Chem. Eng.,

VIRGIL COBLENTZ, Chairman of the Verein Deutscher Chemiker.

COMMITTEE OF ARRANGEMENTS: *Treasurer*, MORRIS LOEB, 273 Madison Ave., New York; *Chairman*, I. F. STONE, 100 William St., New York; *Secretary*, CHARLES F. MCKENNA, 50 Church St., New York.

## BOOK REVIEWS AND NOTICES.

Hygienic Laboratory—Bulletin No. 58. Dec., 1909. Digest of Comments on the Pharmacopoeia of the United States of America and National Formulary. By MURRAY G. MOTTER and MARTIN L. WILBERT.

This volume of 523 pages represents a complete digest of the literature selected from all available sources, relating to the Pharmacopoeia and National Formulary for the year ending 1906, issued under the authority of the Surgeon-General and approved by the Secretary of the Treasury. The recognition of these two standard works through the provision of the Food and Drugs Act, in connection with the U. S. Government becoming signatory with other powers respecting the unification of pharmacopoeial formulae, creates for the U. S. Pharmacopoeia and National Formulary a position of great legal importance. Therefore in the coming decennial revision, it is highly important that the mass of comments and criticisms, more especially those bearing on the relations of these works to the law, are in shape readily available. Also during the interval of 5 years new revisions of several foreign pharmacopoeias have appeared which must receive careful consideration in accordance with the agreement between the United States and the Brussels Pharmacopoeial Conference.

As a work of reference for chemists, physicians and apothecaries, this report is highly recommended since there is scarcely a field in which they are interested not reviewed. In the table of contents appear some of the following headings: Legal Status of Food and Drug Law, Standards, Analytical Data (physical constants, thermometry, polarization, apparatus, color standards), Biologic Products, Vegetable Drugs (valuations, ash determinations, alkaloids, physiologic standardization), Pharmaceutical Preparations, International Standards, Foreign Pharmacopoeias, Rules of Brussels Conference, Comments on Official Standards, etc.

The compilers are to be commended upon the thoroughness and care exercised in this task. V. COBLENTZ.

New and Non Official Remedies 1910 Containing Descriptions of the Articles which Have Been Accepted by the Council on Pharmacy and Chemistry of the American Medical Association Prior to Jan. 1st, 1910.

The purposes of this book (256 pp. with index) are explained

in its preface as follows: The Council of Medicine and Pharmacy was established in February, 1905, by the American Medical Association, primarily for the purpose of gathering and disseminating such information as would protect the medical profession in the prescribing of proprietary medicinal articles. In pursuance of this object the Council examines the articles on the market as to their compliance with definite rules which are designed to prevent fraud, undesirable secrecy and the abuses which arise from advertising to the laity. Such articles as appear to conform to the rules are admitted and their essential features are described in this annual publication of the Council. Physicians are to understand that the acceptance of an article does not necessarily mean a recommendation, but that so far as known it complies with the rules of the Council.

Through this means the Amer. Med. Ass'n has endeavored to combat the proprietary medicine evil. The contents embrace practically all of the newer synthetics that have appeared in our market, in addition to organic gland remedies, serums, vaccines and some proprietaries. It is an excellent and authoritative book of reference for the chemist, apothecary and physician since the descriptions, tests of identity and for impurities as well as therapeutics are fully treated. V. COBLENTZ.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### SEMI-ANNUAL MEETING AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The summer meeting of the American Institute of Chemical Engineers will be held at Niagara Falls, N. Y., June 22-24, 1910.

A prominent feature of the meeting will be visits to the interesting chemical industries in this locality.

An important program of papers is being arranged for by the Committee on Meetings.

### COMMITTEE ON RESEARCH PROBLEMS, DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The Committee on Research Problems of the Division of Industrial Chemists and Chemical Engineers realizes that the field open to it is broader than it can possibly cover in its entirety. It feels that it is not within its province to take up specific problems that are of limited interest or that affect merely economic questions of local interest; rather that its work should be on broad lines of questions of general methods of research and of researches that affect the conservation of natural resources by decreasing waste and rendering materials now ignored of use.

We, therefore, ask the members of the American Chemical Society for suggestions of lines on which it is practicable for us to work and that will enable us to be of the greatest assistance. The following seemed to the committee promising ones on which to start, but if we are to succeed in them we must have the coöperation and assistance of the members.

We wish the members to send us statements of the general problems that they are investigating, in order that we may bring in direct communication those who are working on similar lines. We also wish to be in a position to put those who desire advice as to general methods and appliances in direct communication with those who can and will give such information. There are many members of the Society who are so located that they have not access to libraries when they are called upon to make investigations in lines new to them. It will be of great assistance to such men if they can learn who have worked on similar lines and are willing to give them advice and tell them where to look up the particular points they wish to know about. The committee particularly desires to be informed

which members are willing to assist others in this way and on what particular lines.

In a great many cases men have made occasional observations, tests and analyses, which by themselves are only of temporary interest, but if the results obtained by all who have worked on any of these lines were collected and compared, the results would often be of permanent value. As an instance, the collection of routine coal analyses, from which a map was prepared showing the geographical distribution of sulphur and ash in the Welsh coal fields. This map proved to be of great value to the consumers. A similar collection of analyses of our coals, especially if it included the determinations of the fusibility of the ash, would be very useful. The analyses published by the coal companies, and even the Geological Surveys, are often unsatisfactory, as they are usually either those of picked samples or of very large averages that do not correctly represent what the consumer is likely to receive.

In the aggregate the amount of work done by students for their theses is immense, but it is scattered and individual results are often small. The committee believes that if the colleges would coöperate and agree on a list of subjects each year and the results of all the theses on any subject compared, much valuable information would be obtained. In many cases the work done in one year would suggest modifications and extensions of the problems to be taken up the next year. In many cases it is not practicable to publish a thesis, and in many cases they are not of sufficient value to warrant it. Most of them, however, contain some points that are new or interesting, and if a number of those on one subject could be combined they would be well worth publishing, and the men would have the credit for the good work they have done.

If those in charge of such work will let us know whether they consider such coöperation feasible, and if so, how best to bring it about, we, as a committee, will do all in our power to assist them.

(Signed): GEORGE C. STONE,  
W. R. WHITNEY,  
G. W. THOMPSON.

### REPORT ON THE MEETING OF THE SUB-COMMITTEE ON GLYCERINE ANALYSIS AT BOSTON, DECEMBER 29 and 30, 1909.

*Organization.*—Mr. R. E. Devine resigned from the committee a year ago. His resignation, however, has not to date been accepted and inasmuch as Mr. Devine has again taken up glycerine work and has expressed a wish to resume his work in the committee it was thought that he should still be considered a member.

Dr. Hillebrand was informed of the invitations extended to Dr. A. M. Comey and Mr. S. E. Emery and stated that these gentlemen would be officially notified of their appointment. Mr. B. T. B. Hyde requested that Mr. Loveland take his place.

The committee as at present constituted therefore consists of:

A. C. LANGMUIR, *Chairman*,  
ROBERT E. DEVINE,  
J. W. LOVELAND,  
W. H. LOW,  
A. M. COMEY,  
S. E. EMERY.

#### SAMPLING AND ANALYSIS.

Meetings were held at the Hotel Lenox on the afternoons of December 29 and 30, 1909. There were present Messrs. Hyde, Loveland, Low, Comey, Emery and Langmuir.

A general discussion of the methods in use for the valuation of crude glycerine and the results handed in on the analysis of the samples sent out by the chairman, took place. All of those present had had practical experience with both the acetin and

bichromate methods. Some of the members used the acetin method almost exclusively in their work; the others made use of the bichromate process mainly, testing occasional samples by the acetin method. The committee was in substantial agreement as to the details of the acetin process. It had been the experience of those members of the committee who had persevered with the acetin method, that good duplicates were obtainable which agreed with the bichromate on good crudes and distilled glycerines and disagreed on bad crudes. Results obtained independently by members of the committee in the analysis of the pure sample A show that both methods have a tendency toward low results, but that these results are practically identical in the case of pure glycerine. In view of this and the fact disclosed by replies received to the committee's circular letter that a majority of glycerine chemists use the bichromate method and are strongly in favor of it, the committee felt that both methods should be investigated, with the object of recommending the details of each method necessary to achieve the best results and to indicate which process should be employed with impure crudes.

A test which would measure the impurities present and indicate the cases where the bichromate would be unreliable is very necessary. The determination of non-volatile organic impurities leads to discordant results unless conditions are under good control and is not adapted to the general laboratory. The determination of alkali combined with fatty acids is readily carried out and possibly is a guide to the amount of organic impurities present. Messrs. Low and Langmuir undertook to investigate the reliability of this test in various crudes.

The chairman stated that there should be little trouble in reaching an agreement as to the details of the acetin method or the methods of testing dynamite glycerine and advised that the brief time at their disposal be devoted to a thorough discussion of the bichromate method in order to reconcile differences and lay out lines of research.

Correspondence received by the chairman revealed a chaotic condition with respect to the bichromate method, each chemist using modifications of his own with widely different methods of purification and oxidation. Considerable work is necessary to decide which of these modifications are erroneous or superfluous and to evolve a method embodying the best features of the methods submitted.

*Sampling from Drums.*—No attempt should be made to include salt in the sample, which must be free from solid deposits to insure agreement among chemists. Drums should stand bung up, to permit salt to settle. The sample is taken with a glass tube as large as can be closed by the thumb and long enough to reach to the bottom of the drum, as stratification is possible. If salt is felt the tube must not be pushed into the salt. In removing the tube, the glycerine adhering to the outside is stripped by drawing through the fingers. Every drum is sampled. Sample is delivered into a large preserve jar with compression top, which can be warmed and shaken to mix sample.

Any salt left in the drum after dumping is not washed out, but is weighed with the tare and placed at the disposal of the seller.

For analysis a large weight should be taken and reduced by aliquoting.

For purification silver sulphate, basic lead acetate, combinations of the latter with silver oxide or carbonate, and copper sulphate are in use.

Mr. Langmuir promised to make a study of the relative effectiveness of silver sulphate and basic lead acetate.

The committee considered evidence to the effect that silver oxide showed a tendency to oxidize glycerine, particularly in alkaline solutions and concluded that silver carbonate or sulphate would be a superior agent for the removal of chlorine.

On account of its superior solubility silver sulphate should be more effective than the carbonate in removing chlorine. Mr. Low will make a comparison of the two reagents in this respect.

The chairman cited experiments showing that the salt left after treatment with lead acetate alone, did not exceed 3 milligrams in the portion taken for oxidation in the Richardson and Jaffe method and that no measurable error was produced in this way. If silver salts are not required in the removal of chlorine there is no object in adding them unless the purification is more complete, or the precipitate more easily filtered.

Mr. Low's experiments with salt led him to a different conclusion. Mr. Low agreed to test the effect of the small amounts of salt which would escape the lead acetate in the bichromate oxidation mixture.

Mr. Low and the chairman were also at variance in regard to the action of the acetic acid in the small amount introduced by the lead acetate, upon the oxidation mixture and it was agreed that each repeat his experiments.

Mr. Emery undertook to make a comparison of copper sulphate and lead acetate in samples to be sent him by Dr. Comey.

Dr. Comey will make a study of the effect of varying basicity of the lead acetate in the purification of glycerine to determine whether glycerine is retained in the precipitate when the acetate is strongly basic.

In regard to the oxidation, the chairman believed that the problem consisted in so adjusting conditions that all of the glycerine and a minimum of the fatty acids present be oxidized. A reaction may be considered analytically complete if the time is equal to twenty times that necessary to carry it half way. As all know, the oxidation of glycerine is so rapid as to be almost violent when concentrated sulphuric acid is added to the glycerine bichromate, and it would appear that the glycerine oxidation is complete in a few minutes unless intermediate products are formed which are but slowly oxidized. This is an important point and the chairman undertook to determine the minimum time necessary to effect the maximum oxidation with C. P. glycerine.

Once established this time should not be exceeded, in order to reduce the error due to oxidation of fatty acids. This reaction, as may be observed by mixing acetic acid with the bichromate mixture, is a slow one, but may occasion considerable error if the time be unduly prolonged. The speed of a reaction is halved by every 10° C. reduction in temperature. The chairman believes that this error should be diminished to a fourth, as may be done by carrying on the oxidation at 80° C., provided the oxidation of glycerine may be completed at this temperature. He agreed to test the effect of the lower fatty acids in this way.

Independent work on the above lines by other members of the committee is advisable.

If carbon monoxide or formaldehyde are formed and escape in the gases, an error is produced which goes to offset that due to fatty acids. Dr. Comey agreed to test the gases evolved for the above impurities.

A difference in results is possible by varying the initial temperature of oxidation. This may be done by adding dilute sulphuric acid instead of concentrated as in Comey's method. Mr. Loveland will experiment on these lines and will also determine whether there is any difference between delivering the glycerine to be oxidized at the bottom of the hot bichromate sulphuric mixture or adding sulphuric acid in the usual way to the bichromate-glycerine mixture.

The committee agreed that bichromate was the best standard. It should be pulverized and dried at 110–120° C.

The most desirable standard is anhydrous glycerine or glycerine of known strength as determined by an accurate specific gravity table. Messrs. Comey, Low, Emery and Langmuir



will attempt this winter to establish the gravity of anhydrous glycerine.

It was decided to meet again in June and it was hoped that the above research work would be far enough along at that time to enable the committee to make final recommendations.

The chairman had prepared three samples for analysis, marked A, B, and C. "A" contained 76.02 per cent. of anhydrous glycerine, 4.00 per cent. sodium chloride, 1.00 per cent. potassium sulphate, 0.50 per cent. sodium carbonate and 18.48 per cent. of water. These amounts were carefully weighed and thoroughly mixed. The glycerine was prepared from a high-grade C. P. product. The water was first expelled by heating *in vacuo* until the glycerine was boiling freely. The first third of the distillate was rejected. The second third only of the glycerine run was taken. The vacuum was about 12 mm. and special precautions were adopted to exclude moisture. The specific gravity of this glycerine at 15.6°/15.6 C. was 1.2651, not corrected to *vacuo*. "B" was a light-colored soap lye crude of good quality. "C" was a dark-colored soap lye crude obtained by thoroughly mixing a number of low-grade samples of domestic and foreign crudes.

## BICHROMATE METHOD

Analyst.	Sample A.	Sample B.	Sample C.	
1.	75.85	80.18	78.99	Silver carbonate and basic lead acetate
2.	75.63			
	74.99	80.24	78.77	Silver sulphate and basic lead acetate
	78.11	79.63	78.83	
	79.65			
3.	74.07	79.23	78.00	Silver sulphate over night.
	74.81	79.19	78.70	
	74.30	79.29	78.40	
	74.16	78.86	78.36	
4.	75.35	79.30	77.70	Silver oxide and basic lead acetate.
5.	75.86	82.37	79.75	Silver sulphate only.
	80.29			
6.	75.36	80.61	79.98	Basic lead acetate hot, double precipitation.
7.	75.49	80.16	78.96	Silver oxide and basic lead acetate
	75.49	80.12	78.88	
	75.47	80.09		
	75.48	80.18		
8.	76.20	81.09	79.32	Basic lead acetate 5 hours' digestion.
	75.97	80.77	79.09	
9.	75.80	79.85	79.00	Basic lead acetate and silver acetate 20 minutes' digestion.
	75.40	80.01	79.00	
	75.90	79.68		

## ACETIN METHOD

Analyst.	Sample A.	Sample B.	Sample C.	
1.	75.40	80.13	78.79	Special precautions taken to avoid carbonic acid.
			d79.46	
7.	75.60	80.18	78.36	Small amounts carbonic acid may be present.
	75.48	80.28	78.15	
10.	74.34	78.96	76.91	
	74.41	78.96	76.72	
9.	75.65		78.66	No carbonic acid present.
	75.69		78.61	
Sp. gr. 15/15.....	1.2475	1.2905	1.2948	Analyst 1
Non-volatile 160° C.	55.36%	10.16%	12.48%	" 1
Ash.....	5.16%	9.25%	9.48%	" 1
Non-volatile organic.....	0.20%	0.91%	3.00%	" 1
Hypsulphites.....	None	Trace	0.09%	" 1

The following chemists, all of whom have had special experience in glycerine analysis, have tested the three samples and sent their reports to the chairman, who takes this opportunity to express his appreciation of the work they have done and the interest they have shown: W. H. Low and E. F. Lyford, of the Cudahy Packing Co.; W. D. Richardson, E. F. Scherulov and R. H. Fash, of Swift & Co., Chicago and Ft. Worth; C. L. V. Zoul, of Procter and Gamble, Cincinnati; J. W. Loveland and

G. A. Horne, of Babbitt & Co.; A. M. Comey, Fleming and S. E. Emery, of the Du Pont Powder Co.; F. S. White, E. Nordell and Y. H. Kooyumjian, of Marx and Rawolle; R. E. Divine, Detroit; J. F. Hinckley, New York; Stillwell and Gladding, New York, consulting chemists.

The bichromate equivalent of 1 gram of glycerine varies from 7.462 to 7.486 in the reports received. In order to place the figures on the same basis the chairman has recalculated the results to the equivalent 7.456, in accordance with the 1910 atomic weights.

NOTES: (a) Analyst 3 was told that his results were low. The tests were run again and the percentages opposite a obtained. This chemist frequently allows the glycerine to stand over night in contact with the silver chloride formed by the action of silver sulphate on the salt.

Mr. W. H. Low obtained materially lower results in the analysis of crudes with silver oxide as a purifying agent, when the mixture stood any length of time, the silver chloride being reduced to metallic silver. Cazeneuve<sup>1</sup> prepared glyceric acid by the action of silver chloride on glycerine in alkaline solution. Unless the glycerine is carefully neutralized these conditions will exist when silver sulphate is permitted to act all night. With silver oxide the error should be more serious as caustic soda is formed as a by-product, which, however, would be removed if lead acetate were subsequently added.

(b) Analyst 5 was asked to run sample B again with the result opposite b.

(c) Three chemists working independently.

(d) Analyst prefers this test.

(e) Sample A contains 0.50 per cent. soda which probably produced polyglycerols in contact with the glycerine at 160° C. Analyst 7 was unable to obtain good results on this sample until the alkalinity was removed.

(f) Two chemists working independently.

Results by the acetin method agree well with the exception of 10 and are uniformly low in the case of "A." Sample C is quite impure as only low-grade crudes were used in its preparation. This is confirmed by the high amount of organic impurities found by analyst 1 above, yet the difference between the acetin and bichromate methods is not marked.

ABSTRACT OF REPLIES RECEIVED TO THE CIRCULAR SENT OUT BY THE SUB-COMMITTEE ON GLYCERINE ANALYSIS.<sup>2</sup>

A. C. LANGMUIR, Chairman.

E. COOK & Co., London:

The acetin method gives results below the truth. In order to get accurate results the very greatest care and attention are necessary in all the details. We employ it in cases of divergence as a check test on our regular method—the bichromate. We prefer the latter method, which is standard and which can be easily adhered to in all details. Such a method is a necessity in a laboratory handling a large number of samples of varying raw and finished products. Silver oxide appears to give more accurate results. We measure the bichromate solution as near as possible to 60° F., allowing 15 to 20 seconds to drain. We agree that the bichromate is the most reliable basis, but prefer to standardize each time against Mohr's salt which is kept in solution in full bottles in a dark room.

Sampling is very important. Drums should be well rolled. If it is possible to feel much salt at the bottom of the drum sampling cannot be satisfactory.

D. & W. GIBBS, London, G. N. Petty, Chemist:

Modified Hohner Method: Clarification effected with copper sulphate and caustic potash. Oxidation—2 hours at 180° F. The bichromate is kept in neutral solution for in this condition its strength does not change appreciably. It is standardized

<sup>1</sup> Analyst No. 4 re-analyzed sample C using silver acetate instead of silver oxide and obtained 78.85 per cent.

<sup>2</sup> *Compt. rend.*, 122, 1206

<sup>3</sup> See *This Journal*, 1, 268.

against C. P. glycerin whose strength is determined by specific gravity, using Gerlach's table.

The acetin method is less satisfactory with crude glycerines. The salts present require a higher temperature to keep the mass fused and this sometimes causes a loss of vapor from the top of the air condenser. The end point when neutralizing with 2 per cent. caustic soda is often extremely difficult to determine, probably due to the presence of acid salts such as those of aluminum. This may also occur with lime compounds in saponification crudes. Unless troublesome precautions are taken to exclude carbon dioxide, uncertain results may be obtained during the final titration with acid.

Neither method is quite satisfactory from the distiller's point of view as with low-grade crudes much more glycerine is sometimes shown by analysis than can be recovered by distillation.

J. CROSFIELD & SONS, Warrington, England, J. Allan, *Chemist*:

Weigh 1.2 to 1.5 grams crude glycerine into a 100 cc. flask. Fill flask half full of distilled water, add 1 cc. 10 per cent. caustic soda and then 3 or 4 cc. 10 per cent. copper sulphate solution (or sufficient to neutralize the caustic soda). Fill to the mark with cold water, shake and filter. Twenty-five cc. of the filtrate are added to 40 cc. standard Hehner bichromate in a beaker; add while cooling 17 cc. sulphuric acid. Cover and heat for 2 hours at 80° C. When cool, determine the excess of bichromate in the usual way, using a fresh, strong solution of ferricyanide as indicator.

In this modification chlorides are not removed. Under the conditions laid down and with a temperature not exceeding 80° C. there is no loss of chlorine or chromium oxychloride. Furthermore, at this temperature all the glycerine is oxidized and practically none of the lower fatty acids are acted on.

LEVER BROS., LTD., Port Sunlight, England:

We are in complete accord with you as to the inconvenience caused through differences in results obtained by various chemists due in greater part to the want of standard and uniform methods of analysis and manipulation. We shall bring forward at an early meeting of the glycerin association the question of appointing an expert committee representative of buyers and sellers to consider the whole matter and come to an agreement as regards the British trade. When this has been done no doubt the agreement of a universal scheme with American and Continental makers can be arrived at more simply.

J. LEWKOWITSCH, London:

Refers to the 4th edition of his Chemical Technology for his views. Further comment superfluous.

RICHARD WHEN & SONS, LTD., London:

We should be glad to know of the establishment of a standard method; we also have had experience of different results from the same glycerin which makes it difficult to have confidence in the present variety of methods.

TYSON RICHMOND & JONES, Liverpool:

We use the acetin method.

T. & H. SOWERBY, London, F. E. Fry, *Chemist*:

Modified Hehner with some of Richardson & Jaffe's modifications. We have come to rely on the standard value of pure bichromate. The duration of the heating has been thirty minutes and we prefer a considerable excess of bichromate to be present. A preliminary blank is essential. 7.464 grams bichromate correspond to 1 gram glycerin.

PRICES PATENT CANDLE CO., LTD., Battersea, J. McArthur, *Chemist*:

Take average of the bichromate and acetin methods as the former overestimates and the latter underestimates the amount of real glycerin present. Bichromate, recently fused, is taken as the standard. 7.486 grams equal 1 gram glycerin. The

Mohr salt solution in each time standardized against the bichromate.

The crude glycerin is purified by basic lead acetate only. A weighed portion of the filtrate, about 25 cc., is oxidized with a weighed portion of standard Hehner acid bichromate, using about 50 per cent. excess over the glycerin present and an equal volume concentrated sulphuric acid is added. Heat 2 hours in a water bath, cool, dilute, add a weighed excess of acidified Mohr salt solution and titrate back with dilute bichromate one-tenth the strength of the standard bichromate solution.

The acetin method is carried out as recommended by Lewkowitsch except that 5 grams instead of 3 grams dry sodium acetate are used. We have experienced no serious difficulty in carrying out this method. In the case of candle crude the bichromate and the acetin methods give results agreeing within 0.2 to 0.5 per cent. but with less pure glycerin the difference may be 1 per cent.

With dynamite glycerin we take the specific gravity and obtain the per cent. from Gerlach's table.

The following results were obtained:

Specific gravity at 60° F.	Glycerol by acetin method Per cent.
1.2625	98.08
1.2640	98.70

PROCTER & GAMBLE, Ivorydale, C. L. Van Zoul, *Chemist*:

We use the bichromate method with some of our own adaptations.

Weigh 5-10 grams glycerine. Dilute to 500 cc. and take 50 cc. into a 250 cc. flask. Just neutralize the alkalinity with 1 : 4 sulphuric acid. Add powdered silver sulphate a little at a time until the precipitate coagulates, add water to the mark, shake, stand over night or filter and draw off 50 cc. into an Erlenmeyer. Add 25 cc. bichromate and 15 cc. conc. sulphuric acid. Heat 2 hours in a steam bath. Titrate with iron ammonium sulphate in the usual way. Run a blank at the same time.

Bichromate solution—74.88 grams with 150 cc. conc. sulphuric acid in 1000 cc. Iron ammonium sulphate made by dissolving two 12-oz. beakers of Baker's salt in 2000 cc. water. Standardize by the blank. Silver sulphate is made from pure silver nitrate by dissolving 200 grams in water and adding 66 cc. conc. sulphuric acid while stirring vigorously. Cool, decant and wash five times with ice water. Place in funnel and wash three times. Exhaust dry, place in large dishes in hot air bath, then powder fine and preserve in dark bottles. It should have no odor of nitric acid.

To determine organic impurities we would advise the determination of total Na<sub>2</sub>O in the ash as well as the free Na<sub>2</sub>O in the sample.

Na<sub>2</sub>O free:

Take 10 grams, dilute with 50 cc. water, add phenolphthalein and an excess normal acid, boil down to half the volume and titrate back with normal caustic factors equals 0.031. This Na<sub>2</sub>O includes free and that combined with light volatile acids.

Na<sub>2</sub>O total in ash:

Burn 5 grams in a large platinum dish, add a drop of ammonium nitrate solution. A small amount of alcohol added assists the burning off. Weigh the residue for ash. Dissolve in water and titrate with methyl orange for total.

Na<sub>2</sub>O:

The difference showing the combined Na<sub>2</sub>O to non-volatile acid and a comparison of the three Na<sub>2</sub>O percentages gives a fair valuation of the glycerine.

*Dynamite Glycerine.*—Salt is determined by dilution and titration in the usual way. This is as accurate as is necessary.

*Specific Gravity.*—We use the pycnometer at 15/15° C. though at times 20/20° C. and apply a correction. We would

advise the adoption of a uniform temperature for a standard at about 20° C.

Use a pycnometer with a thermometer and do not close until the temperature inside and that in the outside water bath is the same.

**Sampling.**—When salt is deposited in the drums we leave some in the drums and weigh it in the tare so that the sample which is taken from each drum with a dipper represents the net weight of stock taken out of the drums.

If a too great excess of silver sulphate is added in removing salt, particularly in spent lyes, an insoluble compound of silver and chromic acid separates from the cooled oxidation mixture, causing high results. The silver salt may be filtered out, dissolved in hot, dilute sulphuric acid, and titrated against iron, when the difference will be made up.

PROCTER & GAMBLE, Kansas City, M. Brayton Graff, *Chemist*: The acetine method does not appeal to me as a practical method for a laboratory where large numbers of determinations are to be run in the shortest possible time. The bichromate method lends itself more easily to a systematic rapid yet accurate working. I find it easier to get concordant results. Duplicates within  $\frac{1}{10}$  per cent. are perfectly possible. With regard to incomplete oxidation to carbon dioxide, I should advise the same dilution on all determinations, say 50 cc. solution containing 0.05 to 0.1 gram glycerine with 25 cc. bichromate and 15 cc. conc. sulphuric acid. Digest 2 hours in steam bath. Lower fatty acids reduce bichromate somewhat but the amount is negligible if one avoids the introduction of acetic acid by the use of silver sulphate instead of lead acetate.

The bichromate is taken as the standard and we measure it out with a pipette at a standard temperature.

A determination of the sodium carbonate in the ash of soap lye crudes is a good indication of the amount of organic impurities.

Burn the crude to a coke, take up with hot water, breaking lumps, filter and take aliquot parts for titration for salt and carbonate of soda which will constitute most of the ash. Burn the filter and coke for insoluble ash.

CUDAHY PACKING CO., W. H. Low, *Chemist*:

The average results of the bichromate method to be described are very reliable. Our average agrees well with the averages of foreign chemists although there are some serious differences in individual cases. Good checks, however, are no indication that the actual determination of glycerol is correct. Polyglycerols or glycol would produce results far from the truth, as the glycol in particular appears to be on the increase and the bichromate method is almost valueless for such glycerines. We examine most glycerines by both the bichromate and acetin methods, the difference between the results indicating glycol or polyglycerols. We have come to think more highly of the acetin method and believe that its results are nearer to the truth than the bichromate; much nearer if glycol and polyglycerols are present, although of course still high.

My assistant has made eight acetin tests a day with ease.

**Sampling.**—Errors here cause more differences than any modifications of the bichromate test. With excessive salt we do not attempt to include it in the sample but test a filtered sample for glycerine and estimate the salt. The sample is well stirred with a long iron wire flattened at the end and any deposit is loosened and well mixed.

Fifteen grams are weighed and washed into a 250 cc. flask and diluted to the mark. Twenty-five cc. are then pipetted into a 100 cc. flask. Rinse in freshly precipitated silver carbonate prepared from 0.5 gram silver sulphate in 100 cc. water by adding 3.5 cc. *N* sodium carbonate, settling and washing once by decantation with 100 cc. water. This amount applies to the average soap lye crude.

Agitate, stand 10 minutes and add 2.5 cc. basic lead acetate

(see Wiley's "Agricultural Analysis," Vol. III). Agitate well, stand 15 minutes, dilute to the mark, adding 0.2 cc. for the volume of the precipitate, filter through a dry filter and take 25 cc. into a 250 cc. volumetric flask. Add  $\frac{1}{2}$  cc. conc. sulphuric acid to precipitate lead. The lead sulphate is not removed; about 42.5 cc. bichromate solution are pipetted into a weight burette and after weighing is added to the purified glycerine solution. Approximately 12.5 cc. excess bichromate solution should be present. 15 cc. conc. sulphuric acid is now added with agitation and the flask, loosely covered, is placed for 2–2½ hours in a boiling water bath. Dilute, cool, make up to the mark, shake and settle out lead sulphate if time permits. Fill into a burette and titrate against Mohr's salt solution (20 cc. = 0.01 gram glycerol).

Silver carbonate is safer than silver oxide, particularly with impure crudes. It is very necessary to remove all chlorine. Using 15 cc. sulphuric acid in the oxidation mixture and 2 hours time is very much safer than the quick digestion of Richardson and Jaffe with 25 cc. acid and 20 minutes. In the latter case oxidation is rarely complete as is shown by the fact that gas is still escaping from the solution after 20 minutes and the results obtained average lower. This may be offset by the oxidation of acetic acid. In the former case acetic acid is not oxidized.

Silver oxide on standing with crude glycerine, particularly if impure, gives rise to false results for the silver chloride first precipitated is more or less decomposed, silver being thrown down and chlorine going into solution.

When using silver carbonate the purified filtrate should always show that an excess of lead has been used, otherwise the results will be too high. Strong bichromate solution contains 74.64 grams and 150 cc. conc. sulphuric acid per liter. Ferrous ammonium sulphate 30 grams with 50 cc. sulphuric acid per liter. Compare on every series of tests with dilute bichromate prepared from 12.5 cc. of the above by diluting to 250 cc. We standardize the bichromate against iron wire.

**Note by Mr. Low:** We are now weighing out the solid bichromate instead of having a standard solution to work with. We get the best C. P. bichromate, pulverize it finely and dry for several days in a large vacuum desiccator under almost perfect vacuum over strong sulphuric acid. As a check we often standardize with our standard iron wire, but there is practically no difference shown and we only do this as a precaution with a new lot of bichromate after preparation.

#### The Acetin Process:

1.5 grams crude, 3 grams recently fused sodium acetate and 7.5 cc. acetic anhydride are heated in a 60 cc. flask with ground glass joint and return condenser. A gentle boiling by an electric stove is maintained about 1½ hours. Cool somewhat, pour 50 cc. of water free from carbon dioxide into top of condenser. Heat and agitate until solution is complete. Cool now completely and filter rapidly, using 4–6 inches of suction into a 850 cc. Jena glass Erlenmeyer. Wash up to 300–400 cc., add 2 cc. (1 per cent. in 50 per cent. alcohol) phenolphthalein and titrate  $\frac{1}{2}$  normal caustic. The end point is a marked change in the color but should not be a full pink. Small drops should be used at the end from a Mutter's oil burette. Add 25 cc. 10 per cent. caustic from a burette, cover and digest in the steam bath,  $\frac{1}{4}$  to  $\frac{1}{2}$  hours. Run a blank on 10 cc., this being about the excess present with the same volume of water. Cool and titrate excess alkali with *N* sulphuric acid.

Crystallized sodium acetate fuses in its own water, solidifies again and should then be carefully further heated in a platinum dish until completely melted, avoiding overheating. Every precaution must be taken to avoid loss of triacetin by volatilization; no serious delays should occur to allow hydrolysis after dilution and good agitation must be kept up during titration. Water free from carbon dioxide should be used. It is best



obtained by distillation and condensation under 27–28 inches of vacuum.

Standard alkali is made by mixing C. P. caustic with its own weight of water and after standing cold filtered through asbestos. The filtrate is diluted with pure water.

Standard sulphuric acid is made up by Marshall's specific gravity process.<sup>1</sup>

*Ash and Non-volatile Organic Matter at 160° C.:*

Take 16 $\frac{2}{3}$  cc. of the original solution of the 15 grams crude in 250 cc. (= 1 gram of the crude) in a 45 cc. platinum milk dish and heat gradually in oven until 160° C. Maintain at this temperature as nearly as possible. This is important. The dish should be level. When dry, cool, add a little water to just dissolve the residue dry in steam bath and return to oven where it is maintained until practically constant weight is found.

Obtain the ash by igniting gently until white or gray. The difference gives the non-volatile matter to which too little attention has been paid in this country.

DU PONT DE NEMOURS POWDER CO., Eastern Laboratory,  
A. M. Coney, *Dir.:*

Both the bichromate and acetin methods are used.

*Bichromate Method:*

A portion of the well mixed sample is transferred to the weighing bottle by a short length of  $\frac{1}{4}$  inch glass tubing filled with glycerin by suction and wiped free from glycerine on the outside while withdrawing 1.5 to 2.0 grams are required. Rinse into a 500 cc. volumetric flask with 40–50 cc. water. Add a slight excess moist silver oxide and then a slight excess basic lead acetate. Shake and dilute to 500 cc. Filter through a dry filter and take 100 cc. of the filtrate in a 500 cc. flask. Add a weighed amount of dry bichromate, which has been gently fused, ground and dried at 110° C., in amount equal to ten times the weight of the glycerine, as this excess is necessary to insure complete oxidation. Add 75 cc. dilute sulphuric acid 1:2; acidification directly with strong acid sometimes decomposes a little glycerine.

Heat exactly 2 hours in a steam bath. This is sufficient for refined glycerine, and any further reduction which may occur in some instances must be due to impurities. Cool rapidly, dilute to about 300 cc. and titrate the excess of bichromate by iron ammonium sulphate added in the dry condition from a weighed amount in a weighing bottle. The salt should have been ground through a No. 30 mesh and well mixed. The addition of the salt is continued until the first appearance of the blue color on a spot test with fresh ferricyanide solution 0.01 to 0.03 per cent. strength.

The value of the iron salt is determined in terms of bichromate by titrating 3.5 grams bichromate in 75 cc. dilute sulphuric acid 1:2 and dilution to 300 cc. with the iron salt as above, running the test under the same conditions as to volume and depth of green color due to chromium sulphate.

A saturated solution of the tri-basic acetate is used. 5 cc. of this to 1.75 grams of crude glycerine are never exceeded.

The bichromate is taken as the standard. 1.0 gram = 0.13397 gram glycerine.

*Acetin Method:*

Essentially that outlined by Hehner in 1889. 1.5 grams of the crude are dropped into 3 $\frac{1}{2}$ –4 grams dry sodium acetate in a 100 cc. dry Jena flask from a Lunge pipette, the weight being found by the loss in weight of the pipette. 7 or 8 cc. acetic anhydride are now added and the mixture gently boiled with return condenser 1 $\frac{1}{2}$  hours. Cool and add 50 cc. hot water through the condenser tube. Heat carefully with cautious but thorough shaking until solution is effected. This sometimes requires as much as five minutes and is continued until

a slight froth or a few bubbles persist on the surface for two to three seconds. Cool somewhat, add a few cc. more water through the tube, remove the flask and filter into a 750 cc. Erlenmeyer, wash well, cool well, and neutralize carefully the free acid with 2.5 per cent. caustic and phenolphthalein. (Continue as described under Low's method—*Chairman.*) Make a blank run on 25 cc. of the strong caustic.  $N/2$   $H_2SO_4$  is used throughout.

If when fusing the sodium acetate, the salt is in any way charred, the end point is interfered with. It is not as sharp and in addition a solution of the charred salt shows a yellowish color which deepens that due to the impurities of the glycerin.

The heating under the return condenser should be only sufficient to cause a gentle boiling; a higher rate sometimes results in a decided darkening of the mixture.

A blank is always made with each new bottle of acetic anhydride, following exactly the same scheme as is used when making a glycerine determination. With all samples yet met with, a correction must be applied for a small amount of an ester-like substance which is present and is saponified with the acetin by the caustic soda. In some cases the error amounted to 0.7 per cent. glycerine.

The percentage of carbonate contained in the caustic used is not of any great importance provided it is reasonably low and provided none is lost between neutralization and final titration. Absorption of carbon dioxide after adding the strong caustic should be avoided. All water added after neutralization of the free acetic acid or to the strong alkali blank should be free of carbon dioxide.

In regard to the danger of hydrolysis after dilution referred to by Hehner, results obtained when neutralization was not effected until thirty-five or forty minutes after solution of the acetin agreed with the bichromate on the same glycerine.

SWIFT & CO., Chicago, W. D. Richardson, *Chemist:*

My opinion and that of some six or eight chemists, who have been in my employ is that the bichromate is the only satisfactory method to use and that the acetin method is thoroughly unsatisfactory and unreliable.

In recent times we have taken the potassium bichromate as a standard although we sometimes standardize against iron wire.

*Solutions.*—Potassium bichromate 74.86 grams and 150 cc. conc. sulphuric acid per liter. Standardize against iron wire or Mohr's salt. It expands 0.05 per cent. for every 1° C.

*Ammonium Ferrous Sulphate.*—59.725 grams with 25 cc. conc. sulphuric acid in water and make up to 500 cc. Make it up fresh daily.

*Subacetate of Lead.*—To 170 grams lead acetate in a weighed 10-inch dish add 800 cc. boiling water. Add 100 grams finely powdered lead oxide and boil  $\frac{1}{2}$  hour, keeping up the volume. Cool and add enough water to make the product weigh 1000 grams. Filter in well-covered funnel and keep well stoppered, 1 cc. = 0.13 gram sodium chloride.

Weigh 5 grams of the glycerine into a 500 cc. flask, dilute slightly and add 10 cc. lead acetate solution. Shake, let stand  $\frac{1}{2}$  hour and make up to 500 cc. Settle or filter through a dry filter and measure 50 cc. into a 300 cc. Erlenmeyer. Add 50 cc. of the bichromate solution from a pipette and 25 cc. conc. sulphuric acid and digest the covered flask 5 hours in the steam bath. Run a blank under the same conditions with 50 cc. bichromate solution.

Remove from bath and pour into a 10-inch porcelain dish containing 1000 cc. water and 25 cc. conc. sulphuric acid. Titrate with the Mohr's salt solution until two drops of the oxidation mixture produce a blue color with dilute ferricyanide on a spot plate.

N. K. FAIRBANK CO., St. Louis, C. B. Cluff, *Chemist:*

In my own work I use the Hehner method, omitting the use

<sup>1</sup>J. Soc. Chem. Ind., 1899, p 4; 1902, p 1508

of the weak bichromate which adds nothing to the accuracy of the work.

On C. P. glycerine this method showed 98.10 per cent. as against 98.15 per cent. from the specific gravity and Gerlach's table. I have always standardized my solution against iron wire but I also find that the bichromate itself is an equally good standard. I use a stock solution, taking the temperature at the time of each test applying the proper correction for this factor. Basic lead acetate alone is enough. We use no silver oxide.

I think the important point to work on is the determination of the concentration temperature and time of heating necessary to get accurate results, also whether silver oxide is necessary or advantageous.

A specific gravity table should be adopted as a standard and think Gerlach's would be satisfactory to practically all chemists.

With regard to the acetin method my experience shows that it gives results about  $\frac{1}{2}$  to 2 per cent. lower than the Hehner method on soap lye crude, and it is too tedious and inconvenient for ordinary laboratory use. On very low-grade samples this method may give better results but in such cases the end point is so indistinct as to greatly interfere with the accuracy of the work.

I have made some experiments as to the effect of varying concentration during the oxidation, and find that considerably higher results are obtained by concentrating the solution to about 25 cc. before the adding bichromate. There is often a difference of 1 per cent. between the tests made in a volume of 100 cc. and 25 cc. However, I do not consider the higher results thus obtained as more accurate, as it is generally understood that this process as ordinarily carried out gives results higher than the truth in any case.

J. EAVENSON & SONS, Camden, N. J., G. D. Hulley, *Chemist*: 1.5 grams crude glycerin are weighed in a small weighing bottle. Wash into a 4 oz. Erlenmeyer flask with 25-30 cc. water, neutralize to litmus with sulphuric acid and add an excess of moist silver oxide. Stand forty to sixty minutes, filter, make up to 200 cc. and take 50 cc. portions in duplicate in No. 2 beakers. Add 50 cc. conc. bichromate solution from a pipette and then 20 cc. conc. sulphuric acid. Heat on a steam plate fifty to sixty minutes and determine the excess bichromate with ferrous sulphate solution standardized by tenth-normal bichromate tested against iron.

Iron 0.11742 = glycerine.

B. T. BABBITT, G. A. Horne, *Chemist*:  
*Bichromate Method*:

Weigh about 0.8 of a gram in small beaker and transfer to  $\frac{1}{2}$  liter flask with water. Add 0.3 of a gram of silver sulphate to ppt. chlorides, giving a swirling motion to the flask, in order to effect precipitation of silver chloride without causing any froth on the liquid. Then add 3 or 4 cc. basic lead acetate solution, and fill flask to the mark. Agitate thoroughly. Filter after allowing ppt. to subside, discarding filtrate until it runs through perfectly clear. Accurately measure 50 cc. of filtrate with a standardized pipette into an eight-ounce Erlenmeyer flask; add 25 cc. of concentrated sulphuric acid. Measure from a burette 50 cc. of a standard solution of potassium bichromate, 1 cc. of which equals 0.002 of a gram of glycerine, into the flask containing sample, and heat for one hour in a steam bath. Titrate excess of bichromate with a solution of ammonium ferrous sulphate, approximately equal in strength to the standard potassium bichromate, using a very weak solution of potassium ferricyanide as indicator.

This standard solution of potassium bichromate is readily sensitive to one drop. It is particularly necessary to add the sulphuric acid before the bichromate, as it has been found that

a small amount of lead chromate is thrown down when the bichromate is added first.

#### *Acetin Method*:

Weigh one gram of crude into a 75-100 cc. narrow-neck flask having a ground joint to connect with reflux condenser. Add 3 grams of anhydrous sodium acetate and 6 cc. acetic anhydride. Connect with condenser and boil  $1\frac{1}{2}$  hours. After cooling, pour warm water through condenser, disconnect flask, and pour contents into a 250 cc. flask, filling to the mark. Pour at once through a dry filter, and carefully pipette 50 cc. of filtrate into a 12-oz. flask. Neutralize acetic acid with half-normal caustic soda. Run into the flask 30 cc. of half-normal caustic soda (from a burette), five drops of phenolphthalein solution and boil 20 minutes. Titrate excess of alkali with half-normal hydrochloric acid, calculate glycerine from amount of caustic soda required to saponify the tri-acetin. A blank test should be made on each new bottle of acetic anhydride. It is absolutely essential to have caustic soda solution perfectly free from carbonate. Water used in process should first be boiled.

*Notes*, by Mr. Horne:

"Having given the acetin method as described by Hehner a thorough trial, and also modification as described above, I am convinced that the latter is much easier to manipulate, and gives a finer end point, particularly in the case of very dark crudes or foots. In working with 0.2 gram sample on the titration instead of  $1\frac{1}{2}$  grams, no difficulty whatever is experienced, due to coloring matter, even in very impure crudes.

"The filtering of the diluted acetin is very rapid, and the neutralization of free acetic acid, which only requires from 25-30 cc. of half-normal caustic soda, seems to me a marked improvement over the tedious process of the original method, where frequently 125-150 cc. are required. It would seem to be more scientific as well as convenient to saponify the acetin with the half-normal alkali instead of the strong 10 per cent. solution, and no blank is required regularly, as the half-normal caustic soda does not change.

"Have made some experiments which show that the acetin diluted with cold water practically suffers no change by hydrolysis, even after several hours."

MARX & RAWOLLE, A. C. Langmuir, *Chemist*:

Our method is that described in *The Journal of the Society of Chemical Industry*, 1898, p. 330, by Richardson and Jaffe, except that a few modifications have been made in the interest of greater accuracy.

Weigh 25 grams of the thoroughly mixed sample and transfer to a 250 cc. flask. Dilute to the mark with distilled water. Mix well and take 25 cc. with a pipette against which the flask has been standardized. Add 1 to 3 cc. of basic lead acetate<sup>1</sup> for a saponification and 7 cc. for a soap lye crude. Filter through a 12.5 cm. paper for a saponification or a 15 cm. for a soap lye, into a 250 cc. flask. Wash with cold water, stirring up the precipitate thoroughly. To the filtrate, about 225 cc., add 5 cc. of sulphuric acid (1 : 3) and 12 cc. of saturated silver acetate solution. The latter serves to remove the small amount of chlorine present as lead chloride. Dilute to 250 cc., mix well and filter through a dry 15 cm. paper. Take 20 cc. of the filtrate for analysis. The pipette should have a narrow orifice and should check against the 250 cc. flask last used.

To avoid the error involved in measuring out 25 cc. of strong bichromate solution, we prefer to weigh the bichromate for each test. It is pulverized and dried at 110° C. and is taken as pure instead of standardizing against iron. Hehner's solution contains 74.86 grams potassium bichromate and 150 cc. of conc. sulphuric acid to the liter. We, therefore, weigh  $\frac{1}{40}$  of 74.86 or 1.8715 grams of bichromate and dissolve it in 25 cc.

<sup>1</sup>Brit. Pharm.

of dilute, warm sulphuric acid (150 cc. to a liter). It is convenient to have a weight made of exactly 1.8715 grams and weigh the separate charges of bichromate on a tared watch glass, adjusting the weight to within a milligram, which with practice can be very quickly done. In the long run time can be saved by this method as no attention need be paid to temperature or to standardizing the bichromate solution.

After cooling, 20 cc. of the purified glycerine solution as above are run in. The beaker is covered and 25 cc. concentrated sulphuric acid is run in slowly. Complete the reaction by heating for 20 minutes in a boiling water bath. Dilute, cool by placing the beaker in running water and finally dilute to 250 cc. Mix, pour the solution into a burette and titrate against 25 cc. standard Mohr's salt solution, freshly made, using potassium ferricyanide as an indicator. The titration should follow closely after the oxidation, as dust will gradually reduce the bichromate, giving high results. All apparatus must be scrupulously clean and free from grease or dust.

Taking the molecular weight of glycerine at 92.08 and bichromate at 294.5 we have 1 gram of glycerine equals 7.4627 grams bichromate. This quantity of bichromate is equivalent to 59.6611 of Mohr's salt, taking the molecular weight of the latter at 392.4. We have taken the bichromate equivalent at 7.486 in order to agree with Hehner. Mohr's salt is rarely pure, and we therefore standardize it against bichromate as follows:

Dissolve 5.9661 grams of Mohr's salt in 40 cc. of 15 per cent. sulphuric acid. Add 0.7360 gram bichromate dissolved in 20 cc. water. Titrate the mixture with a solution of 100 milligrams bichromate dissolved in 100 cc. water, using ferricyanide as indicator.

To get the end point make two titrations and add to the first at the end 2-3 cc. excess of bichromate solution. Use drop tests obtained from this solution to compare with spot tests obtained in the second titration. Our Mohr's salt required 5.9 cc. Therefore 5.9661 grams called for  $0.7360 + 0.0059$  or 0.7419 gram bichromate— $0.7419 : 0.7486 :: 0.5966 : x = 0.6020$  gram.

For the regular analysis, therefore, we weigh 6.02 grams Mohr's salt and dissolve it in 250 cc. of water containing a little sulphuric acid. Take 25 cc. portions for the titration.

A blank should be occasionally run on the water and reagents. To 7 cc. of the basic lead acetate add 5 cc. of the dilute sulphuric acid and 12 cc. of the silver acetate solution, dilute to 250 cc. and filter. Run 20 cc. of the filtrate into a solution of 0.6730 gram of bichromate in 21 cc. water and 4 cc. sulphuric acid. Add 25 cc. conc. sulphuric acid and heat 20 minutes in the boiling water bath. Dilute, cool, dilute to 250 cc. and titrate against 25 cc. Mohr's salt solution as above. Not more than the equivalent, 27.8 cc., should be required. Repeated tests have shown that the acetic acid introduced by the 7 cc. of lead acetate causes no measurable reduction of the bichromate.

The basic lead acetate<sup>1</sup> is made as follows: boil a mixture of 142 grams of lead acetate, 99 grams of litharge and 568 cc. water a half-hour and then make up to 591 cc. Filter.

When the above weights and proportions of crude glycerine are taken, the percentage is given by the following formula:

$$\text{Per cent. glycerine} = 125 - 1250/\text{cc.}$$

#### STILLWELL AND GLADDING:

Weigh out as quickly as possible exactly 5 grams of the substance on a balanced watch glass. Wash it into a 250 cc. flask with warm water, using about 50 cc. Add a half gram of silver acetate which has previously been triturated with a little water in a mortar. Shake frequently during 15 minutes.

Add water until flask contains 200 cc. Then add subacetate of lead in slight excess. Fill up to mark with water, insert glass stopper and mix thoroughly. Filter through a dry filter paper, take 10 cc. (0.20 gram) of the solution and wash it into a beaker holding about 300 cc. and using about 100 cc. water. Add about 15 cc. concentrated sulphuric acid and 20 cc. of potassium bichromate solution. Add water until the beaker contains from 175 to 200 cc. Cover with a watch glass and place in boiling water for two hours, stirring with a glass rod from time to time. Remove from bath and allow to cool. Add about 50 cc. water to replace that which has evaporated. Titrate with ferrous sulphate spotting on porcelain plate with potassium ferricyanide until the blue color just appears.

#### Potassium Bichromate Solution:

74.5600 grams 100 per cent. potassium bichromate and 150 cc. conc. sulphurous acid are dissolved in water and made up to 1000 cc. 1 cc. of this solution is equivalent to 0.01 gram glycerine.

#### Ferrous Sulphate Solution:

240 grams of C. P. ferrous sulphate and 50 cc. conc. sulphuric acid are dissolved in water and made up to 1000 cc.

#### Standardization:

Standardize the ferrous sulphate against the bichromate solution whenever the test is made.

#### ROBERT E. DIVINE, Detroit:

Weight 2 to 3½ grams, rinse into a wide-mouthed flask with 100-125 cc. hot water, heat nearly to boiling and add an excess of a 2 per cent. solution of Merck's tri-basic lead acetate, 10 cc. being usually sufficient, heat about ten minutes, filter and wash well with hot water. Wash lead precipitate back into the flask and heat nearly to boiling, add  $N/1$  caustic soda, about 1 cc. for each cc. lead acetate used, heat until ppt. is dissolved.

Now add  $N/1$  sulfuric acid in amount equivalent to the caustic soda. The reprecipitated lead salts now free from glycerine are filtered and washed with hot water. The filtrates are combined, acidified with dilute sulfuric acid and evaporated until they can be transferred to the proper flask (200 cc. for 2 to 2½ grams crude and 250 cc. for 2½ to 3½ grams), excess of silver sulphate is added and solution mixed, made up to volume, filtered through dry filter and 25 cc. run into a solution of 3.7308 grams bichromate crystals in 50 cc. water, 30 cc. conc. sulphuric acid added and heated 2 hrs. in boiling water bath.

The bichromate is weighed out for each test.

#### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

Those desiring information concerning the prices at which rare elements and special compounds can be furnished provided a considerable market is assured, and the extent of the available supply, are requested to indicate their needs to the Chairman of this Committee as soon as possible. All are invited to make suggestions regarding the scope of the work which has been undertaken.

Prompt responses to this request will greatly facilitate the work of the committee and render needless repetition in correspondence unnecessary.

GELLERT ALLEMAN, *Chairman*,  
Swarthmore, Penna.

Committee to confer with manufacturers regarding the supply of, and prices for, rare elements and special compounds.

<sup>1</sup>*Brit. Pharm.*



## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

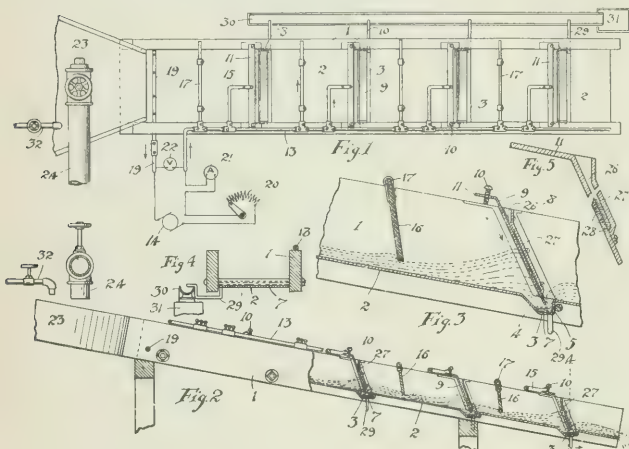
Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**947,957. Process of Recovering Fine Gold.** JAMES H. ALLING, San Francisco, California. February 1, 1910.

The object of this invention is to provide a process for the recovery of very fine particles of gold, silver, and platinum.

In practicing the process there is employed a sluice box of the kind shown in the accompanying illustration.

This sluice box is sloped at a greater angle than are the sluice boxes used for the recovery of gold in the ordinary processes.



In the bottom of the sluice box is a continuous amalgamating plate formed at suitable intervals into pockets or troughs. Each pocket is formed with a rear wall having a considerable slope, nearly 45 degrees, to the vertical, a front wall sloping slightly backward from the vertical, and a bottom substantially horizontal. In each pocket is placed a sufficient quantity of mercury. The sides of the sluice box are formed with oblique grooves inclined rearwardly upward, and across the sluice box extend anode amalgamating plates with their edges in the grooves. The lower edges of the plates extend to within a short distance, say  $\frac{1}{8}$  of an inch, from the upper surface of the mercury in the troughs or pockets. The height of each plate can be adjusted by means of adjusting screwed through lips extending from the plates over the sides of the sluice box, the screws resting on the tops of said slides.

Extending along one side of the sluice box is an electric conductor connected to the positive pole of an electric current generator. This conductor is connected by conductors with the several plates, which thus serve as anodes for currents of electricity.

In addition to the anode plates there are provided swinging carbon anodes suspended from bars extending across between the tops of the side of the sluice box, substantially midway between the anode plates.

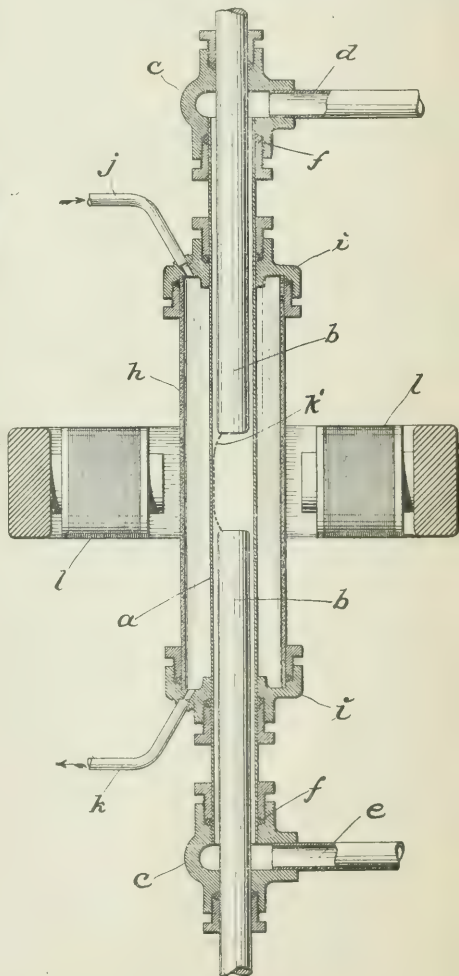
The cathode plate is connected by a wire to the source of the electric current.

The material, having been first finely pulverized, is fed by a chute into the top of the sluice box. At the same time there is fed a sufficient quantity of water, about 4 tons to 1 ton of material, and through a pipe is fed a small proportion, about 1 to 1000, 2000, or more parts, of a mixture consisting of aqueous solutions of potassic cyanid and mercuri chlorid.

The patentee claims that by his process he has been able to save over 95 per centum of the values of material containing finely divided gold, which cannot be saved by ordinary processes.

**948,372. Process for Producing Oxids of Nitrogen from the Air.** FRANCIS I. DU PONT, Wilmington, Delaware. February 8, 1910

This process consists in subjecting air contiguous to a cooling medium to the action of a moving arc whereby the high temperature of the air produced by the arc is immediately and rapidly reduced, thus producing, the patentee states, the best possible



conditions for the production of oxids of nitrogen from the air.

In order to produce a continuous and not disconnected arc, the air container is of silica or other highly refractory material which is not a conductor of electricity. The air is passed through a tube formed of silica in which are electrodes between which an arc is formed. Surrounding this silica tube is a glass tube through which a cooling medium, such, for instance, as a cooling liquid, is passed, thus forming a water jacket, as it were, for the silica tube. Surrounding this cooling tube, in proximity to the arc, is a rotary magnetic field, which rotates the arc around the inner surface of the silica tube. The air passing in contact with the inner surface of the silica tube is, by the rotating of the arc, highly heated, and as soon as the arc passes from any portion of the air, such air is immediately subjected to cooling action and its temperature rapidly reduced.

The accompanying illustration shows the apparatus in which the process is carried out.

In operation air is forced in through the passage, into the zone between electrodes. When the arc is produced and the rotary magnetic field is in action, the arc is caused to rotate around the inner periphery of tube *a* coming in contact and acting upon successive portions of the air in contact with said tube. The arc at once highly heats such air. As soon as the arc passes from any portion of the air, such air being in contact with the wall of tube *a*, which is subjected at all times to the action of the cooling medium in tube *b*, has the high temperature produced by the arc immediately and rapidly reduced. By this operation the action of highly heating and cooling any given portion of the air is practically simultaneous, thus more perfectly and with greater certainty forming the oxids of nitrogen from the air. The air is forced in at a pressure from atmospheric to one hundred pounds. The oxids of nitrogen thus produced are the lower oxids and with the air unacted on pass along the tube in the space between the electrode and the wall of the tube escaping by the passage *d* from which they may be led into water where they are converted into nitric acid, in the ordinary manner.

949,474. Process of Refining Iron. FREDERICK W. HAWKINS AND GEORGE F. KEY, Detroit, Michigan. February 15, 1910.

It is the object of this invention to provide a process which is suitable for the refining of iron which, in its crude state, has a high percentage of impurities requiring for their elimination different treatment. For example, iron which contains both silicon and phosphorus, or silicon, sulphur and phosphorus cannot be directly treated in an open-hearth basic-lined furnace, for the reason that the linings would be destroyed by the reactions of the silicon. On the other hand, such metal cannot be refined by the Bessemer process, as this does not extract the phosphorus, and sulphur.

With this process the iron is first treated in a receptacle or furnace to eliminate the impurities which will yield to oxidation and subsequently, but in direct continuation of this first treatment, the metal is subjected to a second treatment, with a basic material, in another furnace or chamber, which removes the phosphorus and sulphur. In the latter step and preferably in both steps of the process all portions of the metal are subjected to uniform treatment by atomizing or breaking up the molten mass into minute particles, this being preferably accomplished by a blast of

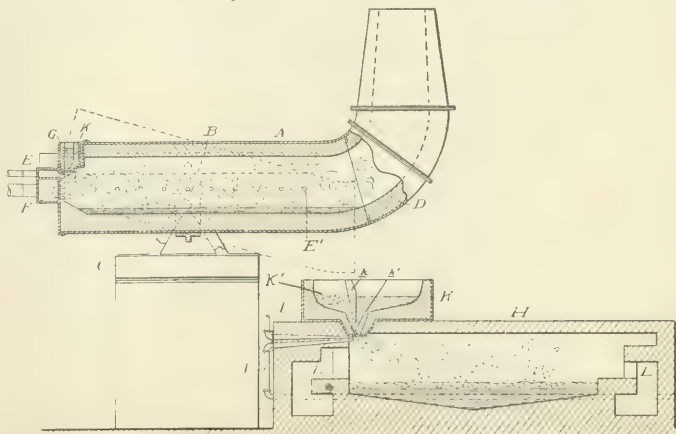
dry steam, or of dry steam and air, the latter being preferably pre-heated.

With the apparatus shown the refining process is carried out as follows: A suitable quantity of the crude molten metal is first poured into the well *G* while the furnace *A* is arranged in its horizontal position. At the same time air and steam, either in conjunction or separately, as conditions may require, are forced through the tuyeres *E* and *F* so that metal dropping from the well may be blown into fine particles and scattered throughout the length of the furnace *A*. During the passage of the small particles of metal through the atmosphere within the furnace, a large percentage of the silicon, manganese and carbon will be removed by oxidation. The metal will then collect in the bottom of the furnace where it remains until the entire charge has passed therein. The furnace *A* is then revolved on the turntable *C* and tilted upon the trunnions *B* so as to lower its open end over the well *K* on the furnace *H*. This will permit the molten metal within the furnace *A* to be discharged into the well *K* from which it is fed through the restricted passage into the path of the air and steam admitted through the tuyeres *I* and *J*. This will a second time atomize the molten metal with the result that the remainder of the silicon, manganese and carbon will be oxidized.

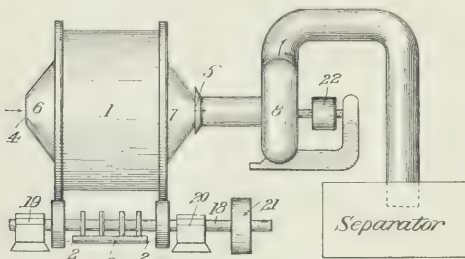
The bottom of the furnace *H* is covered with a layer of comminuted basic material which is heated to a high temperature by burning gases entering the furnace chamber from end ports *L*. This comminuted basic material forms a filter bed through which the minute particles of molten metal are obliged to percolate and in so doing the metal is brought into intimate contact with the basic material which extracts the phosphorus and sulphur. Thus the metal which finally passes through the filter bed and collects in the bottom of the furnace *H* is purified both from silicon, manganese and carbon, and also from the phosphorus and sulphur.

950,115. Process of Removing Tin from Scrap. CHARLES J. REED, Philadelphia, Pennsylvania. February 22, 1910.

This process is intended for the separation of mixed metals, particularly of tin from tinned metals, as for example iron. The process comprises three steps, namely: first, removing the tin in pulverulent or subdivided form from the iron or other coated metal by agitating a charge containing the tinned metal and a subdivided foreign body; second, removing the pulverized tin from the foreign body and from the detinned iron by means of a current of air, steam or gas; third, removing the foreign body from the detinned iron.



In carrying out the first step in the process advantage is taken of the fact that metallic tin is rendered weak, friable and easily pulverized by heating the charge, preferably to about the melting



point of tin. The subdivided foreign body used to pulverize or wipe off the fused or softened tin may be any substance which is infusible and non-volatile under the conditions of use.

The amount of the foreign body added to the charge is also variable within wide limits, one to ten and one to one-tenth having been used.

The second step of the process consists in removing the pulverized tin from the foreign body and detinned iron by means of a current of air, steam or gas. This operation may be carried on simultaneously with the pulverizing operation or as a subsequent operation. This is preferably done simultaneously by causing a current of air to pass through the apparatus in which the pulverizing takes place. This current of air is then projected into a separating or settling chamber in which the particles of tin settle by gravity on the floor, or the air is passed through a series of bags or screens of textile or other suitable material in which the tin is collected in the form of a powder of metallic tin or oxid of tin. The air or other gas may be heated to the proper temperature, if desired.

The third step in the process consists in screening the residual mass on a screen capable of allowing the subdivided foreign body to pass through, while rejecting the detinned iron or the principal part of it. The foreign body may then be used over again indefinitely.

A convenient form of apparatus for carrying out the process is shown in the accompanying drawings, in which 1 represents a hollow cylinder of iron or steel mounted to revolve on rollers 2, carried by a shaft 18, supported in bearings 19, 20 and driven by a pulley 21. The drum is mounted over a suitable source of heat, diagrammatically shown as a series of gas burners, and has two openings 4 and 5 at the apexes of terminal cones 6 and 7. The opening 4 may be used for charging in the tinned iron and foreign body and also for discharging the detinned product.

8 represents an exhaust fan driven by a pulley 22 and adapted to cause a suction current of air through the drum and fan in, the direction indicated by the arrows.

**950,116. Process of Treating Ores and Metals.** JAMES HENRY REID, Newark, New Jersey. February 22, 1910.

According to this process, the ore is first melted and reduced, preferably through the medium of the electric arc, the carbon of which effects a reduction. A gaseous reagent is then passed about the molten stream of the resultant metal to treat the same, the character of the treatment depending on the nature of the reagent.

In the accompanying illustration, an embodiment of the apparatus for carrying out the process is shown.

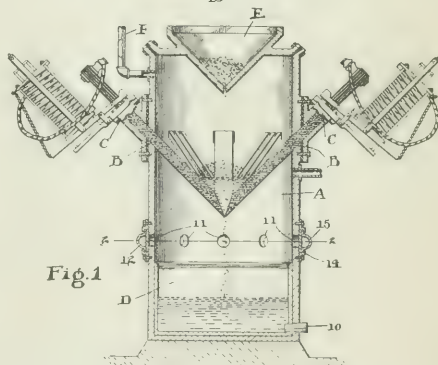
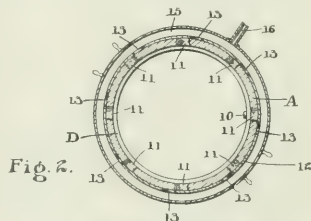
The bottom portion of the furnace in which the stream of molten metal from the arc discharges has preferably a lining *d* of refractory material, and is provided with a suitable dis-

charge aperture 10. The ore is introduced into the furnace through a hopper, *e*, at the top thereof, and an exhaust pipe, *f*, is provided leading from the upper part of the furnace, to suitable exhausting, and if desired, condensing means.

To permit the carrying out of this process, a plurality of apertures 11 are provided in the walls of the furnace below the electrodes, through which the gas may be admitted. The passage of gas through these openings is regulated by an annular plate, 12, having corresponding apertures, 13, which plate is rotatably supported from an annular flange, 14, on the side of the furnace. In order to provide for the admission of different gases to the furnace, an annular conduit is connected to a suitable supply pipe, 16.

In carrying out the process the ore is introduced into the hopper 10 and falls in a continuous stream into the hopper formed by the electric arc and reduced by the carbon of the electrodes, the molten metal and slag dropping through to the bottom of the furnace.

The air or gas to be used in treating the metal is introduced through the apertures 10 and passes around the stream of metal and slag, the movement of the gas being effected by exhausting the upper part of the furnace through the pipe *f*. This suction, as well as moving the treating gas about the stream of ore, exhausts the upper part of the pool of partly reduced ore on the electrodes. The effect of passing the gas will vary with



the character of the ore and of the gas. For instance, an ore might first be reduced by the carbon of the electrode and then air might be drawn around the stream of metal to burn out the impurities. Otherwise, a reducing gas, such as carbon monoxid, might be passed around the stream of metal to complete the reduction started in the arc. It will be observed that this suction, in addition to the stream of gas, also will operate to suck any carbon monoxid or dioxide gas in the metal out of the same.

**950,595. Process of Reducing Metallic Oxide Ores.** HERBERT E. T. HAULTAIN, of Toronto, Ontario, Canada. March 1, 1910.

This process relates to the reduction of metallic oxide ores and especially iron ores for the purpose of obtaining steel directly therefrom.



The general purpose of the invention is to provide a process of reducing such ores by which they may be successfully treated in a finely divided condition and which is especially adapted for use with an electric furnace.

In carrying out this process there is utilized an electric furnace having a receptacle of suitable capacity at the bottom to form a bath of molten material.

The ore if not already in the condition of magnetic iron sands is crushed or ground in a finely divided condition. The ore is then treated in a concentrator to separate as far as possible its earthy components. The ore is then so fed into the furnace preferably mixed with a suitable powdered flux as to produce a shower of discrete particles, in which condition the ore is most readily permeable by the reducing agents and is most readily heated. The furnace is so arranged that the ore meets with no

and carbon and it is therefore usefully employed without producing any deleterious effects.

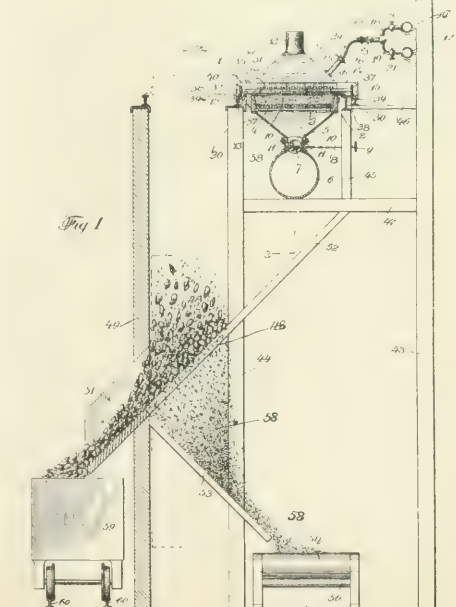
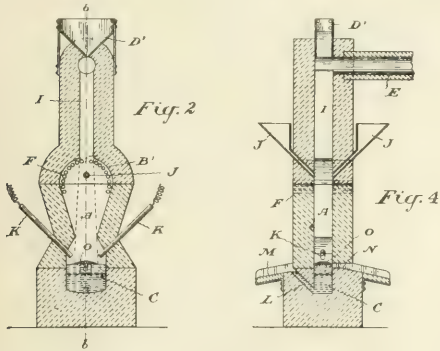
The reactions which take place are stated to be as follows: The shower ore is first calcined and heated as described and after it has passed the calcining portion of the furnace, enters a reducing atmosphere due to the introduction of the shower carbon. By the joint action of the carbon monoxide and the solid carbon the ore is deoxidized and falls into the bath of molten material in the condition of pasty metallic particles mingled with slag. In the bath at, or adjacent to, its surface, the metal is melted and the slag separates collecting on the surface of the bath. This bath has a sufficient capacity to contain a considerable proportion of the daily output of the furnace, and the molten metal is withdrawn from the bath gradually and preferably continuously to a point remote from the place in which the smelting occurs, preferably at the bottom of the bath. This withdrawal is best effected by carrying a suitable conduit from the bottom of the receptacle up to the level of the bath exterior to the furnace. Through this conduit the metal gradually flows off to suitable receptacles. This retaining of the molten metal and its gradual withdrawal equalized any inequalities in the output, which is very important since the proportion of carbon and impurities to the pure metal may be subject to variations, owing to its being continuously produced in small quantities.

The process is carried out in a furnace such as is shown in the accompanying illustration.

951,198. Process of, and Apparatus for, Treating Ores. WALTER G. PERKINS, of Smelter, Nevada, and MARK LAWRENCE REQUA, of San Francisco, California. March 8, 1910.

This invention relates to the treatment of metalliferous ores preparatory to the smelting process, whereby waste of the valuable elements of the ore is reduced to a minimum, and the ore put into suitable condition for smelting in a blast furnace. The best known means of accomplishing this important result,

obstructions from the time it enters the furnace until it reaches the surface of the bath at the bottom. This bath is suitably heated, preferably by electric energy. Into the shower of finely divided ore, preferably intermediate its point of entry into the furnace and the surface of the bath, there is introduced a shower of carbon, also in a finely divided condition. Carbon monoxide is immediately produced by the combination of the carbon with the oxygen of the ore, which carbon monoxide promptly takes up more oxygen from the ore and becomes carbon dioxide, which in turn takes up carbon and is reduced to carbon monoxide again. This process takes place all through the shower. It has been determined by experimentalists that carbon monoxide alone tends only to partially deoxidize the ore and that the best results are obtained by having solid carbon present with the ore to complete the deoxidation. By this process it will be seen that the carbon being actually present in the shower in a solid condition is ready to hand for combination with the finely divided particles of ore which have been practically deoxygenized by the reducing atmosphere supplied by the carbon monoxide. There is necessarily a surplus of carbon employed and a consequent surplus of carbon monoxide produced, which must not be allowed to escape and its heating value lost. At the same time air cannot be introduced into the ore shower after its mixture with carbon to effect this combustion as the formation in the ore shower of carbon dioxide instead of monoxide would result. The patentee therefore shapes the lower portion of the furnace so that it extends laterally on each side of the shower and into this portion of the furnace he introduces air which combines with more or less of the surplus carbon monoxide, producing an intense heating effect which is reverberated against the shower and the surface of the bath of molten material by the walls of the chamber which are suitably shaped to produce the reverberating effect. It will be seen that this air does not contact in any manner with the shower of ore



is to agglomerate or sinter the ore, which is usually in a finely divided state, by subjecting the same to the action of heat from either solid or gaseous burning products, whereby the metaliferous elements will become agglomerated, or sintered into a solid mass or good-sized pieces or lumps, which are then in condition for further treatment, such as smelting as in a blast furnace, without the risk of waste or loss of the valuable elements of the ore.

In the practice of this process the entire body of the ore is subjected to the action of air or other supporter of combustion, and temporarily to the burning products of the source of heat.

The ore to be treated is placed upon a layer of stones disposed upon a support as shown in the accompanying illustration. And is caused to pass through the ore and during this passage burning gas is passed over the surface of the ore. In this way the ore is agglomerated or sintered. The sintered ore is later separated from the unsintered particles by means of a suitable screen.

**951,228. Method of Decomposing Salts.** JASPER WHITING, of Boston, Massachusetts. March 8, 1910.

This invention relates to the electrolytic decomposition of salts by methods involving the employment as cathode of a body of liquid metal or alloy. In methods of this character it has been usual heretofore to maintain a substantially continuous circulation of the cathode, but this practice has, it is claimed, proven objectionable by reason of the tendency of the electrolytically separated metal, as sodium, to become oxidized and to re-enter into solution in the decomposing compartment. For example, in the production of caustic soda by electrolysis

subject to oxidation by the electrolyte undergoing decomposition, resulting in a reduced efficiency of operation.

According to the present invention the liquid metal is maintained in a state of rest during the charging period or period during which the sodium or other metal is deposited therein, but is at appropriate intervals transferred by gravity to a region of oxidation, the denuded or purified metal being thereafter returned to the decomposing compartment. In the preferred embodiment of the invention the alloy or amalgam from the decomposing compartment is permitted to flow through the oxidizing compartment in contact with carbon surfaces and an oxidizing electrolyte.

The accompanying illustration shows apparatus in which the process may be carried out.

**951,272. Obtaining Petroleum Products.** HERMAN FRASCH, of New York, N. Y. March 8, 1910.

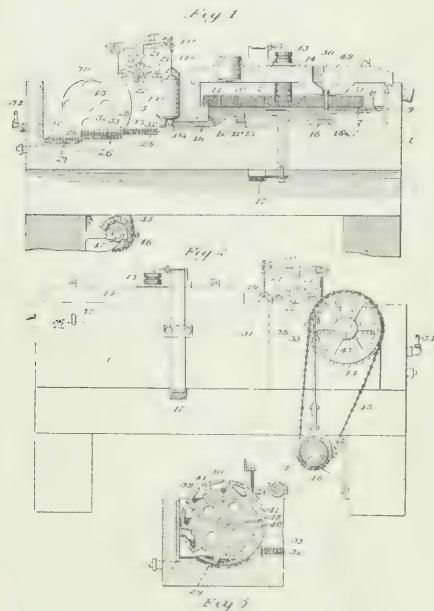
This is a process of obtaining burning oil (kerosene) from petroleum of the nature of that obtained from the wells near Beaumont, Texas, and from other kinds of petroleum.

On subjecting Beaumont petroleum to fractional distillation (with or without cracking) and subjecting the entire distillate which comes over between the ordinary temperature limits of burning oil (say, from 250-600° F.) to treatment with sulphuric acid of 66° B. (followed by the customary washing with water, and with caustic soda solution, and again with water), the resulting product will be colorless and of a mobility to climb a lampwick; but it will smoke when burned in ordinary petroleum lamps, especially if the flame should be turned low. The raw distillate shows the same smoky flame. The patentee claims to have discovered that such distillate is composed in part only of smoky hydrocarbons and that these and the non-smoking hydrocarbons which accompany them in distillation can be separated from each other by the differentially solvent action of an appropriate menstruum, such as methyl alcohol or ethyl alcohol, not only to a useful extent, but sufficiently to obtain from such smoky distillate a non-smoking burning oil whose hydrocarbons have the same range of boiling points as those of said smoky distillate. The invention consists in the processes of subjecting part at least of either or both of said illuminating oil fractions of Beaumont or other petroleum, as above mentioned, to the action of a menstruum, such as methyl alcohol or ethyl alcohol, which has a different solvent action upon the non-smoking from that which it has upon the smoky hydrocarbons of said burning oil fraction of Beaumont petroleum, and thereby obtaining the results stated. The menstruum may be applied to all or to any desired part of either or both of said illuminating oil fractions before or after the separation of the same from other fractions or parts of the petroleum; but the application would best be made after such separation, the oil treated being in the form of an appropriate distillate. The distillation of the crude oil may, in any case, be performed with or without cracking.

In addition to giving an oil of less ratio of carbon to hydrogen than the oil treated, the separation which is effected by the differentially solvent menstruum also results in an oil of greater ratio of carbon to hydrogen; and this more highly carbonaceous product can be utilized for burning as fuel or for other appropriate purpose.

The solvent action of methyl or ethyl alcohol is greater on the smoky hydrocarbons (or those having a higher ratio of carbon to hydrogen) than on the non-smoking hydrocarbons (or those having a lower ratio); but it is evident that a menstruum having the reverse differential action might serve to separate the two kinds of hydrocarbons; and it is believed that a differential solvent in general has now for the first time been applied as indicated.

Nearly anhydrous methyl alcohol is regarded as the best



of aqueous solutions of sodium chloride in presence of a mercury cathode, the sodium amalgam tends to collect at the surface of the mercury cathode and its removal to the oxidizing compartment is only incompletely effected by the flow of the underlying body of mercury; the sodium of the amalgam is therefore

menstruum, but another appropriate menstruum (differential solvent) can be used without exceeding the limits of the invention. As already indicated, ethyl alcohol can be used.

After the desired and feasible separation of the hydrocarbons from each other has been obtained, the menstruum is separated from the hydrocarbons in solution therein in order to obtain purer oil and also to recover the valuable menstruum; and where it and they have sufficiently different boiling points fractional distillation would best be resorted to; but the menstruum separation might be effected in different ways which might vary with the menstruum. Addition of water followed by settling and decantation will separate methyl alcohol or ethyl alcohol from hydrocarbons (of whatever volatility) in solution therein. Methyl alcohol and ethyl alcohol can each of them be separated by distillation from the hydrocarbons which compose the heavier portion of the burning oil fraction of any kind of petroleum. The separated menstruum can be disposed of in any way, but it would best be used over again on a new lot of oil, with or without being subjected to an intermediate treatment.

952,351. Process of Detinning Tin-scraps. WALTER J. PHELPS, of Baltimore, Maryland. March 15, 1910.

It has been demonstrated that tin disintegrates when subjected to extremely low temperatures, as for instance, when brought in contact with liquid air.

Based upon this principle, this process consists in subjecting the tin-coated scraps or tin-bearing material to an extremely low

through the openings at the top of the inner and outer drums, and after the doors of the openings are closed, the inner drum and agitator are rotated for effectively stirring the tin scraps to bring every portion of the tin-coated surfaces in contact with the liquid air which is supplied by the opening of the valve 22. This liquid air acts on the tin in such a way as to destroy the cohesion between the tin particles and the sheet metal coated thereby, and the particles of tin sift through the perforations of the inner drum and are collected in the space at the bottom of the outer drum. After the agitation has proceeded long enough to remove the tin, the door 7 is first opened to allow the tin to drop out into a suitable receptacle. After this is done, the inner drum is opened when the door thereof is at the bottom, so that the sheet metal from which the tin has been removed can be emptied from the apparatus in preparation for the next charge.

## INDUSTRIAL AND TRADE NOTES.

### AMERICAN PATENTS IN ENGLAND.

#### REVOCATION FOR IMPROVEMENTS IN TYPEWRITING MACHINES.

Consul Albert Halstead, of Birmingham, reports as follows concerning the British revocation of letters patent for a typewriting machine manufactured in New York:

A decision of the Comptroller-General of Patents, on December 10, revoked letters patent No. 25382 of 1901 for improvements in typewriting machines, especially referring to an improved key-operating mechanism for the machine manufactured by the Yost Writing Machine Company, of New York. Application was made for the revoking of this patent by Walter Gray Duncan, of Glasgow, on the ground that the article was manufactured mainly or exclusively outside the United Kingdom.

The Yost Typewriter Machine Company is represented in England by the Yost Typewriter Company (Limited), who are the licensees in England for the sale of the typewriters. The company was represented by counsel. Not only was its patent revoked, but it was ordered by the Comptroller-General to pay the costs of the Glasgow applicant, *viz.*, 30 guineas (\$153.29).

This decision is another manifestation of the purpose of British manufacturers to gain every advantage possible under the patents and designs act of 1907, and indicates that many American companies which have developed a large business in the United Kingdom, and which have not undertaken to manufacture in this country the main part of their patented articles sold here, are in grave danger of having their patents revoked and of suffering from the competition of machines made in Great Britain to their designs, machines which, because British-made, in view of the increasing popular prejudice in favor of British-made articles, will become serious competitors.

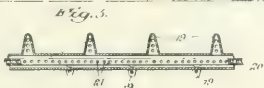
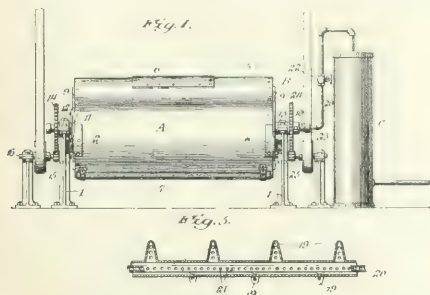
(An abstract of the decision of the Comptroller-General, transmitted by Consul Halstead, is on file in the Bureau of Manufactures.)

## OFFICIAL REGULATIONS AND RULINGS.

### NOTICE OF JUDGMENT NO. 216 FOOD AND DRUGS ACT.

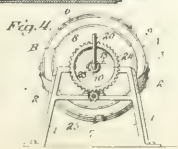
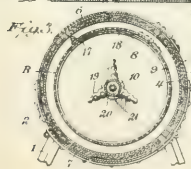
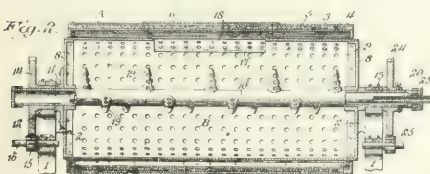
#### Adulteration and Misbranding of Hydrogen Peroxide.

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 14th day of December, 1909, in the United States Circuit Court for the Eastern District of New York, judgment was rendered in the case of the United States *vs.* Eimer & Amend, a corporation, of New York City, prosecuted for a violation of the aforesaid act upon an information in substance charging



temperature, while simultaneously agitating the scraps to cause the tin to separate from the steel or other metal coated by the tin.

In practice, the tin-bearing material is supplied to the inner drum of the apparatus shown in the accompanying illustration





that said defendant filed a guaranty in accordance with the provisions of Section 9 of the said act, which is as follows:

Eimer & Amend,  
Manufacturers & Importers of  
Chemicals and Chemical Apparatus.

NEW YORK, NOV. 14, 1906.

THE SECRETARY OF AGRICULTURE,  
Washington, D. C.

DEAR SIR: We, the undersigned, do hereby guarantee that all the articles of foods or drugs manufactured, packed, distributed or sold by us, including both crude and powdered drugs, alkaloids, chemicals, pharmaceutical preparations, medicinal specialties or proprietary medicines, and any and all articles of foods and drugs as defined by the Food and Drugs Act, June 30, 1906, are not adulterated or misbranded within the meaning of the said act.

Respectfully yours,  
EIMER & AMEND.  
ROBERT P. AMEND,  
*Treasurer.*

Attest  
OTTO P. AMEND [SEAL],  
*Secy.*

Sworn to before me this 25th day of November, 1906,  
[SEAL]

JACOB B. TOCH,  
*Notary Public No. 39, N. Y. C.,*

which said guaranty received a serial number, to wit, 591; and that thereafter the said Eimer & Amend sold and delivered to the Eastern Drug Company, New York City, a certain drug contained in a bottle labeled: "Hydrogen Peroxide 1 pint Eimer and Amend, New York. Guaranteed under Food & Drugs Act, etc., No. 591," which said drug, sold and delivered as aforesaid to the Eastern Drug Company, and afterwards reshipped in its original package by the agent of said company from New York to Boston, Mass., was adulterated in that it was sold under a name recognized in the United States Pharmacopoeia and differed from the standard of quality and purity therein laid down in this, that it contained acetanilid. The information further charged that the said drug was misbranded in that the container thereof, failed to bear a statement of the quantity or proportion of acetanilid contained therein. On December 14, 1909, the defendant pleaded guilty to the information and was fined \$5.

The facts on which the prosecution was based, follow:

On June 8, 1908, an inspector of the United States Department of Agriculture purchased a sample of the drug, labeled as heretofore described, from the Eastern Drug Company, at Boston, Mass., which had been sold and delivered by Eimer & Amend to an agent of said drug company, in New York City, who afterwards reshipped the same to his company at Boston, Mass. The sample was analyzed in the Bureau of Chemistry, United States Department of Agriculture, and found to contain acetanilid. The analysis having disclosed that the said drug was adulterated and misbranded the said Eimer & Amend and the said Eastern Drug Company were duly notified thereof, given an opportunity to be heard, and were heard in regard to said adulteration and misbranding. The Eastern Drug Company having established a guaranty from its vendor, and it appearing that there had been a violation of the act, for which Eimer & Amend was responsible, the facts were reported, on April 16, 1909, to the Attorney-General. The case was referred to the United States attorney for the Southern District of New York, who filed the above information, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., February 21, 1910.

NOTICE OF JUDGMENT NO 220, FOOD AND DRUGS ACT.  
*Adulteration and Misbranding of Turpentine.*

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given of the judgment of the court in the case of the United States vs. 2 Drums Turpentine, a proceeding of libel under Section 10 of the aforesaid act for seizure and condemnation of the said 2 drums of turpentine, lately pending, and finally determined on May 18, 1909, in the District Court of the United States for the District of Vermont by rendition of a decree of condemnation and forfeiture hereinafter fully set out.

The case having come on for final hearing and no one appearing to make any answer to the allegations of the said libel, on May 18, 1909, the court rendered its decree of condemnation and forfeiture in substance and in form as follows:

UNITED STATES DISTRICT COURT FOR THE DISTRICT OF VERMONT.  
UNITED STATES

TWO DRUMS TURPENTINE. }

This cause came on for hearing on the 18th day of May, 1909, and it appearing that said libel was duly served and returned, and no one appearing to make any answer to the allegations in said libel, and it being made manifest that all and singular the premises aforesaid, are true, and within the jurisdiction of this court, it is thereupon ordered and decreed that the said two drums of turpentine in the information and libel mentioned, be, and the same are condemned as forfeited for the causes in said libel and information set forth.

Done in court at Windsor, this 18th day of May, 1909.

JAMES L. MARTIN,  
*United States District Judge.*

The facts in the case were as follows:

On or about January 26, 1909, an inspector of the Department of Agriculture found in the possession of the Dr. B. J. Kendall Company, Enosburg Falls, Vt., 2 drums containing about 112 gallons of turpentine, labeled "Spirits Turpentine," which had been manufactured and shipped to said Kendall Company by the Carolina Pine Products Company, a corporation of Cleveland, Ohio, on December 16, 1908. A sample was taken from this consignment and analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found to contain 35 per cent. of mineral oil. From the aforesaid analysis it appeared that the article was adulterated within the meaning of the act in that it was sold under the name of "Spirits Turpentine," which in common parlance means, and is identical with, "oil of turpentine," a name recognized in the United States Pharmacopoeia, while it differed, in fact, from the standard of strength, quality, and purity laid down therein in that a quantity of mineral oil had been substituted in part for the genuine article; and was misbranded within the meaning of Section 8 of the act in that it was labeled "Spirits Turpentine," whereas it was not, in fact, spirits of turpentine, or oil of turpentine, but a mixture of oil of turpentine and mineral oil.

Accordingly, on January 28, 1909, the Secretary of Agriculture notified the United States attorney for the District of Vermont that the aforesaid 2 drums of turpentine were then in the possession of the said Dr. B. J. Kendall Company, Enosburg Falls, Vt., having been shipped as above stated, and that they were adulterated and misbranded within the meaning of the act. On February 1, 1909, the United States attorney filed a libel in the District Court of the United States for the District of Vermont praying seizure, condemnation, and forfeiture of the said goods, with the result hereinbefore stated.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., February 23, 1910.

# THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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JUNE, 1910.

No. 6

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## EDITORIALS.

### USES FOR RARE ELEMENTS AND SPECIAL COMPOUNDS.

It frequently happens that investigators have put aside and regarded as impracticable, the suggested use of many of the more difficultly obtained chemical elements and compounds, in consequence of the fact that some of these are at present regarded as unavailable—whether such unavailability is the result of either a very limited present supply, or a cost which is prohibitive for the purpose for which the material is desired.

Manufacturers are throwing away many materials which are, at present, looked upon as waste products, and would gladly welcome any suggested use for the same. Through the coöperation of the investigator and the manufacturer, mutual difficulties might be overcome. With a more intimate coöperation, the requirements of the investigator might be supplied by utilizing the waste products of the manufacturer.

The fundamental step towards obtaining this coöperation must be the securing of information concerning the availability of the materials needed and the uses which may be made of them.

When we consider the marvelous improvements recently brought about by the application of electricity to chemical industry, and the accomplishment

thereby of results hitherto unobtained we must be prepared to revise some of our information concerning materials previously regarded only as "museum specimens," and place many of these in the category of substances practical for industrial purposes.

Twenty-five years ago aluminum was not commercially available; to-day, millions of pounds are used in the industries. Only a few years ago, the element silicon was regarded as a curiosity; to-day it may be purchased by the ton—uses having been found for it and convenient methods devised for its preparation. The same might be true of many other elements and compounds, which, at the present time, have but little application.

The Division of Industrial Chemists and Chemical Engineers now has a committee which is endeavoring to deal with this problem. This committee will probably act in the capacity of a clearing-house between the manufacturer and consumers. The committee is composed of former President W. R. Whitney, of Schenectady, N. Y., M. C. Whittaker, of Gloucester, N. J., and Gellert Alleman, *Chairman*, of Swarthmore, Pa. The members of this society are asked for suggestions regarding the scope of the investigations to be undertaken, and we hope that all will aid in this important work.

The committee proposes to publish as complete a list of the prices and availability of the chemical elements as it can obtain, and would be glad to get information to add to this list. It will later probably take up relatively novel or newly available compounds. Such new compounds as come to the notice of members will receive attention by the committee if they are informed of them. GELLERT ALLEMAN.

## ORIGINAL PAPERS.

### A COMPARISON OF THE METHODS FOR DEPOSITING IRON ELECTROLYTICALLY.

By S. A. TUCKER AND E. SCHRAMM.

Received April 1, 1910.

The experiments herein described include the sulphate and chloride baths as these have been used by most investigators. Other electrolytes have been tried without much success, such as ferrous fluor-silicate, but it was considered best to restrict the experiments to the more promising methods and, by comparing them under certain conditions, to decide which would be the most practical for the deposition of metallic iron.

The first solution tried was made by dissolving 200 grams of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in one liter. This gives about 29 grams of iron per liter, or a concentration of 2.9 per cent. of iron. This is the solution as used by Amberg,<sup>1</sup> and probably by Burgess<sup>2</sup> and Hambuechen. The cathodes were clean sheet iron and the anodes consisted of wrought iron bars. The experiments were carried on at room temperature and the results are given in Table I:

TABLE I.—IRON.

Volts.	Amp.	Amp [ ] <sup>dcm.</sup>	Amps. [%]	Lbs. kw. hr.
0.50	0.2	0.176	1.63	4.4
0.56	0.25	0.22	2.02	3.94
0.58	0.30	0.264	2.45	3.76
0.64	0.35	0.308	2.96	3.44
0.68	0.40	0.352	3.27	3.21
0.70	0.45	0.396	3.68	3.12
0.74	0.50	0.44	4.09	2.95
0.90	0.75	0.66	6.04	2.42
1.10	1.00	0.88	8.26	1.98

The current efficiency was determined by inserting a copper coulombmeter in series and gave an efficiency of 95.5 per cent.

The last column in this table shows the effect of increased current density on the energy efficiency. The current was changed temporarily to obtain these figures. In computing the figures for lbs. per kw. hr., the current efficiency was assumed to be the same throughout.

The deposit obtained was silvery white and of a fine crystalline structure. After a while it became badly pitted. The electrolyte kept in condition for a long time; the basic precipitate which formed by oxidation of the air was allowed to collect in the bottom of the vessel. The electrodes were 1 1/2" apart and the current density at the anode was about double that at the cathodes.

Another run was made with the solution and all conditions kept the same as the above except the current density, which was raised to 1 amp. per sq. dcm. The deposit was crystalline and silvery white like that obtained at lower current densities, but showed a greater tendency to form nodules. The current efficiency was nearly 100 per cent., but the voltage drop was 1.2, giving 1.705 lbs. per kw. hour.

A third run was made with ferrous ammonium sulphate solution, with the addition of a small quantity of glycerine. The deposit in this case was smoother and more solid.

Ryss,<sup>3</sup> in his investigations, used a solution containing 200 grams ferrous ammonium sulphate, 50 grams  $\text{MgSO}_4$ , and 4 grams  $\text{NaHCO}_3$  per liter. Ryss claimed that such a solution gave a smoother and thicker deposit of iron than could be obtained with ordinary ferrous ammonium sulphate.

A trial failed to show any improvement in the character of the deposits using such additions, but it did show that the bath had a much greater tendency to form basic precipitate and the time in which it could be maintained in good condition was less than that possible with the simple bath.

The next solution tried was one containing 30 grams  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 21 grams  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  per 100 cc. as described by Kern.<sup>1</sup>

A current density of 1 amp. per sq. dcm. was used. The deposit was dark gray and formed large nodules. At the end of 15 hours the electrolyte was in bad condition owing to the formation of a heavy precipitate.

The net results of the experiments with different sulphate solutions were the conclusion that a solution containing 200 grams per liter of Mohr's salt was the best as regards character of deposit, permanent good condition of electrolyte, and energy efficiency. Attention was next turned to the electrolysis of chloride solutions. The first solution used contained 100 grams  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 50 grams  $\text{NH}_4\text{Cl}$  per liter. The cathodes, as before, being of clean sheet iron and the anodes wrought iron bar. The electrodes were 1 1/2" apart and the bath maintained at room temperature. The current efficiency as determined by a copper coulombmeter was found to be 96.5 per cent. and the following data was obtained:

Time of run 21 1/2 hours.

Average current during run = 0.237.

Average voltage during run = 0.42.

Weight of iron actually deposited, 5.14 grams.

Weight of iron theoretically deposited, 5.32 grams.

Current density during run = 0.304 amp. [ ]<sup>dcm.</sup>

No. watt hours =  $0.237 \times 21 \frac{1}{2} \times 42 = 2.14$ .

1 watt hour = 2.4 grams iron.

1 kw. hour = 5.28 lbs.

The current was varied temporarily to obtain the following readings:

Volt.	Amp.	Amps. [ ] <sup>dcm.</sup>	Amps. [ ] <sup>ft.</sup>	Lbs. kw. hr.
0.40	0.2	0.260	2.42	5.55
0.44	0.25	0.321	2.98	5.05
0.46	0.3	0.385	3.58	4.83
0.54	0.36	0.450	4.18	4.10
0.57	0.40	0.513	4.76	3.89
0.60	0.45	0.577	5.36	3.70
0.60	0.5	0.642	5.97	3.70
0.72	0.75	0.962	8.94	3.08
1.00	1.00	1.280	11.90	2.22

In the next run a solution of double the strength was used, i. e., 200 grams  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 100 grams  $\text{NH}_4\text{Cl}$  per liter. The other conditions were kept much the same as before, excepting that the length of time of the run was increased:

Time of run, 141 hours.

Average current during run, 0.323 amp.

Average voltage during run, 0.67.

Weight of iron actually deposited, 47.145 grams.

<sup>1</sup> Kern, *Trans. Am. Electrochem. Soc.*, **13**, 103 (1908).

<sup>2</sup> Zeit. Elektrochem., **14**, 326 (1908).

<sup>3</sup> Trans. Am. Electrochem. Soc., **5**, 201 (1904). *Electrochem. and Met. Ind.*, **2**, 183 (1904).

<sup>3</sup> Ryss, *Zeit. Elektrochem.*, **12**, 697 (1906).



Weight of iron theoretically deposited, 47.6 grams.

Current efficiency = 99 per cent.

Current density = 0.56 amp. [dm.<sup>2</sup>] = 5.2 amps./ft.<sup>2</sup>.

No. watt hours =  $0.323 \times 141 \times 0.67 = 30.5$ .

1 watt hour = 1.55 grams iron.

1 kw. hour = 3.4 lbs.

The following readings were taken:

Volt.	Amp.	Amps./[dm. <sup>2</sup> ]	Amps./ft. <sup>2</sup>	Lbs. kw. hr.
0.42	0.2	0.345	3.2	5.42
0.50	0.25	0.432	4.01	4.55
0.64	0.3	0.517	4.08	3.66
0.70	0.35	0.604	5.64	3.26
0.72	0.4	0.69	6.4	3.16
0.82	0.45	0.726	6.75	2.78
0.84	0.5	0.862	8.0	2.71
0.90	0.75	1.29	12.0	2.53
0.98	1.00	1.725	16.0	2.32

The following readings were taken:

Volt.	Amps.	Temp.	Current density, Amps./ft. <sup>2</sup>
0.42	1.4	60° C.	15
0.46	1.4	50°	15
0.54	1.4	40°	15
0.64	1.4	30°	15
Taken at start.			
0.36	1.8	60°	19.3
0.34	1.6	60°	11.15
0.32	1.4	60°	15.0
0.30	1.2	60°	12.85
0.28	1.0	60°	10.72
0.26	0.8	60°	8.57
0.24	0.6	60°	6.43
0.22	0.4	60°	42.9
0.20	0.2	60°	2.14
9 days after start.			

The above tables show: that the voltage decreases with increased temperature; and that the voltage decreases as the run proceeds.

Comparison of this process with the others tried shows the best energy efficiency for the ferrous sodium chloride electrolyte working at 50°–70° C.

This bath also gave the best and thickest deposits, the iron being gray and non-crystalline.

ELECTROCHEMICAL LABORATORY,  
COLUMBIA UNIVERSITY.

## STUDIES IN ASPHALT, I.

By C. J. FRANKFORTER.

Received March 23, 1910.

While engaged in testing asphalt for the City Engineer of Lincoln, Nebraska, it was observed that the temperature of the asphaltic mixture, as brought to the street, varied as much as 100° C. maximum to minimum. It was also noticed that the per cent. of bitumen was by no means constant. This seemed a little unusual, and the author decided to experiment and determine if possible the effect of such variations on the paving material.

Literature was consulted, but nothing bearing on the work in mind was found. Paving specifications from Chicago, Brooklyn, New Orleans, and several other large cities, were obtained and consulted. Without exception, these specifications condemned the overheating of an asphaltic cement. Just how hot such material might be heated without injury, or what the harmful effects of overheating really were, was not stated. In all cases the per cent. of bitumen was to be reasonably constant, usually about 10 per cent. of the surface mixture was called for.

Samples of Trinidad, Texas, Cuban Rock, Obispo and Sarco asphalts were collected. Results on two samples only, Obispo and Trinidad, will be presented, since the data on the other brands are as yet insufficient to warrant definite conclusions.

In this paper the author wishes to be distinctly understood as neither recommending nor condemning the asphalts mentioned.

Obispo refined asphalt was a hard substance resembling coal tar in general appearance, but it did not have the "tarry" odor nor was it "sticky" at

A comparison of the two runs given above with the run on ferrous ammonium sulphate solution shows that while the current efficiency is practically the same in both cases, the energy efficiency at any given current density is much higher for the chloride solutions. Comparing the two chloride solutions, we see that the more concentrated solution gives a higher energy efficiency at any given current density.

The physical character of the deposit from the chloride solution was somewhat different from that deposited from the sulphate solutions, being more crystalline than the latter excepting that to which glycerine had been added.

The next electrolyte tried was the ferrous sodium chloride solutions described by E. F. Kern.<sup>1</sup> This was made by dissolving 285 grams FeCl<sub>2</sub>·4H<sub>2</sub>O and 102 grams NaCl per liter, giving 8 per cent. Fe and 4 per cent. Na. The solution may also be made by dissolving iron in the equivalent weight of HCl. The cathode used was thin sheet iron plate  $3\frac{3}{4}'' \times 3\frac{1}{2}''$ . The anodes were bars of wrought iron  $3'' \times 2'' \times \frac{1}{2}''$ . The electrolysis was carried on in a beaker placed on an asbestos pad with a hole cut in it, and heated by placing an incandescent lamp underneath. This kept the temperature between 50° and 70° C.

Previous runs having all shown a high current efficiency of over 95 per cent., it was not considered necessary to use a copper coulombmeter in this run. The object of the run was to:

- (1) Compare the voltage required by this process with the others described.
- (2) To find the effect of heating the electrolyte on the energy required.
- (3) To find the effect of heating on the physical character of the deposit.
- (4) To secure a thick deposit in a short time.

The cathode area was 13.15 square inches.

The electrolyte was kept in condition by adding a little HCl to the bath every day to dissolve the basic precipitate which formed. Water was fed to the bath automatically to make up for evaporation.

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **13**, 103 (1908).

ordinary temperatures. The physical properties of this material varied with the temperature as recorded below:

At 0° C.	Very brittle, broke like glass	No odor.
From 5-10° C.	Slightly less brittle	No odor.
From 20-25° C.	Less brittle, enough tenacity to prevent crumbling	No odor.
From 55-60° C.	Softer, very tough	Faint oily odor.
From 90-96° C.	Began to melt	Stronger odor.
From 115-120° C.	Consistency of molasses	Same odor.
From 135-140° C.	More mobile, luster diminished	Stronger odor.
From 155-160° C.	Very mobile	Very strong odor.
From 180-190° C.	Apparently no change	Strong rancid odor.
At 222-224° C.	Flashed	
At 235-238° C.	Burned	

The Obispo flux was a very viscous greenish-black oil having an odor similar to crude petroleum. Its specific gravity was 0.9894. It flashed at 135-137° C. and burned at 161-162° C.

An asphaltic cement is the material which, when mixed with approximately 90 per cent. by weight of sand, constitutes the wearing surface of an asphaltic pavement. In the case of a natural asphalt containing incorporated native mineral matter a larger proportion would have to be used in order that the mixture might still contain the required 10 per cent. of bitumen.

Asphaltic cement is prepared by fluxing a refined asphalt with some oil, either natural or the petroleum residues from oil refineries. The fluxing is carried on until the asphaltic cement reaches the desired consistency, which is determined by testing its ductility and penetration. After consulting the various paving specifications, a penetration of 40 to 45 at 25° C. was decided on as a standard.

In all these experiments a standard Dow penetration machine was used for the penetration tests. For determining ductility, the author constructed a device with which the material was tested under water at any desired temperature. This apparatus consisted of a zinc-lined water-tight trough, 2 meters long, 13 centimeters wide, and 7 centimeters deep. The inside was given a heavy coating of white enamel paint. This white background enabled the operator to determine the exact moment of rupture of the asphalt. In one end of this trough a small hook was fastened, in the other a small pulley. A reel, manipulated by an ordinary crank handle and carrying a light strong cable, was set up over the trough on a framework near the pulley. This cable ran over the pulley and reached to the opposite end. A standard Dow mold was used in this machine, one end hooked to the end of the box, the other to the cable. When the cable was wound up on the reel the mold was pulled apart. On the bottom of this trough two strips, 1 centimeter high, were fastened just far enough apart to permit the mold to slide between them. They were graduated in millimeters and served as a means of guiding the moving end of the mold, thereby ensuring a straight-away pull.

They also permitted the result of a test to be read off directly. When a test was to be made, the trough was nearly filled with water of the desired temperature, 0°, 25° or 46° C. The mold containing the asphalt was placed in position and allowed to remain twenty or thirty minutes. The water was stirred constantly in order to maintain a uniform temperature in all parts of the trough and to bring the asphalt to the temperature of the water. The reel was then turned until the asphalt pulled apart and the distance it stretched read off directly.

Penetration is recorded in degrees Dow, equivalent to hundredths of a centimeter. Ductility is recorded in centimeters. Both ductility and penetration were determined according to Dow's directions.

Heating the asphalt to a high temperature causes a loss of volatile matter which is accompanied by a decrease in ductility and penetration, though in no definite ratio.

The three temperatures at which these tests are made are supposed to represent approximately the different temperatures a pavement would be obliged to withstand.

When the Obispo refined asphalt was heated for 15 hours at a temperature of 163-165° C. in an air bath, as prescribed by the paving specifications, it lost 2.12 per cent. in weight. The samples weighed 20.0526 and 20.0812 grams, respectively. There was no moisture in this asphalt.

Table I gives the ductility and penetration figures on Obispo refined asphalt, showing the per cent. of loss due to the heating which caused the above-mentioned loss of weight:

TABLE I.—OBISPO REFINED ASPHALT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Before heating	0.2	5.2	20.0	2.0	9.0	33.0
After heating	0.0	0.2	4.2	0.0	0.5	5.0
Loss.....	100.0%	96.15%	79.0%	100.0%	94.44%	84.84%

By fluxing 102 grams of Obispo refined asphalt with 42 grams of Obispo flux, an asphaltic cement was obtained which had a penetration of 45 at 25° C. The ductility could not be accurately determined, as the material persistently adhered to the amalgamated brass plate upon which the mold was poured.

For heating the asphaltic cement an open-air bath arrangement was used. It was constructed in a way which allowed the asphalt container to rest on a false bottom, and this served to keep it out of direct contact with the flame of the burner. It was possible to stir the mixture at all times. Since a thermometer was used for this purpose, it was easy to keep a very close watch on the temperature.

Table II shows the variation of ductility and penetration of the Obispo asphaltic cement after being heated to different temperatures:

TABLE II.—OBISPO ASPHALTIC CEMENT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Heated to 130° C. . .	0.9	33.5	64.6	7.0	39.0	106.0
Heated to 150° C. . .	0.7	27.2	47.8	6.0	29.0	102.0
Heated to 175° C. . .	0.4	19.0	43.0	5.0	25.0	73.0
Heated to 200° C. . .	0.1	15.0	40.0	4.0	21.0	68.0

The ductility here recorded on Obispo is relatively very high. Trinidad and Bermudez, the so-called best asphalts, did not show such high figures. There was this difference. In the case of the two latter asphalts the "body" of the mold stretched and seemed to be "rubbery." With Obispo the material pulled out to a fine thread, and this thread stretched out until it was so fine it could scarcely be seen even against the white background. The "body" in this case showed no tenacity or ductility.

Trinidad refined asphalt was a fairly hard grayish black material with no luster and an odor like freshly plowed earth. At different temperatures it behaved as follows:

At 0° C.	Brittle, crumbled rather easily	No odor.
From 5-10° C.	Slightly brittle, not "crumbly"	Faint earthy odor.
From 20-25° C.	Less brittle, not "crumbly"	Stronger odor.
From 45-50° C.	No apparent change	Same odor.
From 65-70° C.	Began to soften	Same odor.
From 102-108° C.	Entirely melted	Disagreeable odor.
From 120-125° C.	Consistency of molasses, showed stringy or fibrous when stirred	Same odor.
From 150-155° C.	Slightly mobile, odor similar to a mercaptan. (Later qualitative test showed the presence of both nitrogen and sulphur.)	
From 170-175° C.	Very mobile (It is very probable that the incorporated mineral matter prevented this asphalt from showing the same degree of mobility as the Obispo, at approximately the same temperature.)	Very strong odor.
At 208-210° C.	Flashed	
At 233-235° C.	Burned	

For fluxing this refined asphalt a heavy petroleum residue was used. It was a viscous greenish black oil having an odor much like cylinder oil. Its specific gravity was 0.9782.

Table III shows the results obtained by treating the Trinidad refined asphalt in the same manner as the Obispo refined asphalt. The samples weighed 20.2276 and 20.1102 grams, respectively. There was no moisture in this asphalt:

TABLE III.—TRINIDAD REFINED ASPHALT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Before heating. . . . .	0.1	1.8	8.0	0.75	1.5	11.0
After heating . . . . .	0.0	0.2	0.75	0.0	0.2	1.0
Loss. . . . .	100.0%	88.88%	90.63%	100.0%	86.66%	90.9%

The low penetration figures here recorded are accounted for, in part at least, by the presence of mineral matter in the asphalt. This would prevent the needle of the machine from sinking into the material as far as it would otherwise.

Mixing 135 grams of Trinidad refined asphalt with 19 grams of the fluxing oil, produced an asphaltic cement with a penetration of 40 and a ductility of 24 at 25° C. It was necessary to heat this asphaltic cement to 130° C. in order to get a thorough mixture.

Table IV shows the results on this asphalt, when heated to various temperatures:

TABLE IV.—TRINIDAD ASPHALTIC CEMENT.

	Ductility			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Heated to 130° C. . .	1.3	24.0	29.3	4.0	40.0	165.0
Heated to 150° C. . .	0.2	20.8	29.0	4.0	24.0	104.0
Heated to 175° C. . .	0.1	15.6	28.8	3.0	20.0	85.0
Heated to 200° C. . .	0.1	10.6	23.0	2.0	14.0	62.0

Ductility and penetration are the necessary characteristic properties of an asphalt which make it valuable as a paving material. It is these properties which prevent a good asphalt pavement from cracking up in the winter or from becoming so soft in the summer that traffic tends to wear it off the crown of the street into the gutters. So, if these properties are decreased, the efficiency of the asphalt as a paving material would be seriously impaired.

There are certain streets in Lincoln, Nebraska, where the asphalt pavement has deteriorated much more rapidly than it should. At the time these streets were paved the writer was testing the asphalt for the city engineer. The mixing tanks were known to have been heated to a temperature which caused the asphaltic cement to flash and burn. At other times the mixture of asphaltic cement and sand, even after it was dumped into the street from the wagons, showed a temperature above 200° C. The hottest load was 220° C., or 428° F. The exact location of these overheated portions were noted and they are now the worst spots in the street. So in this case the results obtained in the laboratory were confirmed by actual outside observation.

TABLE V.—SOLUBILITY OF OBISPO AND TRINIDAD ASPHALTS.

Solvent used.	Per cent. asphalt soluble.		Mineral matter in asphalt.		Per cent. organic matter soluble.	
	Obispo.	Trinidad.	Obispo.	Trinidad.	Obispo.	Trinidad.
Acetone. . . . .	45.83	14.14	0.43	34.93	46.02	21.73
Benzol. . . . .	99.45	65.01	0.43	34.93	99.87	99.9
Carbon bisulphide. . . . .	99.53	65.05	0.43	34.93	99.95	99.96
Chloroform. . . . .	99.55	60.77	0.43	34.93	99.97	93.39
Ether (ethyl). . . . .	not det.	44.87	0.43	34.93	not det.	68.95
Ligroin (0.710). . . . .	68.88	40.4	0.43	34.93	69.17	62.08

The testing of the solubility of asphalts in various organic solvents was taken up as a preliminary to an attempt to determine the constitution of the so-called "Asphaltene" and "Petroleum." Comparing the last two columns on the right, it would seem that there is a great difference in the constitution of the organic matter of these two asphalts. The per cent. of mineral matter here recorded as constant is the average obtained by various methods both direct and indi-



rect with and without oxidizing agents on many samples of each asphalt.

All the common methods of extracting the soluble portions of an asphalt were tried and set aside. Some were accurate, but too slow; others were fairly rapid but finally divided mineral matter would get away. The following extraction apparatus was found to work better than any of the others, considering both time and accuracy.

Glass tubes 6 centimeters long and 2 centimeters in diameter were obtained. At one end of each of these tubes was a slight constriction which produced a rim (see illustration). Over this rimmed end a C. S. & S. filter paper, No. 589 "Blue Ribbon," was placed. Over this, a C. S. & S. filter paper, No. 575, was laid. The two papers were then firmly and carefully pressed down over the end of the tube and securely fastened with platinum wire. (Copper wire was later found to be just as satisfactory.) The superfluous paper was then clipped off close and the capsule thus formed extracted with the solvent which was to be used on the asphalt. Three or four of these capsules could be prepared at a time and the extraction allowed to proceed while the attention was directed elsewhere.

The tube with its weighed sample was then placed in a Soxhlet extractor having ground glass joints. In the lower part of the Soxhlet a piece of sealed and weighted glass tubing was placed. This tube served a double purpose. It supported the capsule so that about half of it was above the top of the curve of the siphon tube of the extractor, and it displaced a large volume of the solvent thereby causing the apparatus to siphon over more often. The small amount of solvent needed enabled the operator to control easily the volatilization and re-condensation on the sample.

In these tests small samples, never more than 1 gram, were used, as it was found the best results were obtained with samples of such weight and less time was required for extraction. The samples were not pulverized, those powdered showing a tendency to "cake" and clog the filter. This made it more difficult to dissolve out the incorporated organic matter.

With this apparatus very accurate duplicate results were obtained. The amount of mineral matter recovered by evaporating the solution and igniting the residue was not sufficient to cause any appreciable change in the percentage figures.

The writer is indebted to the city engineer for the samples of asphalt and for the paving specifications; also to the Globe Asphalt Company, of Pittsburg, for samples of their products.

The author wishes to take this opportunity of expressing his most sincere and hearty thanks to Chan-

cellor Samuel Avery, of the University of Nebraska, for his kind advice which was offered at the most opportune moments and which proved of so much value.

#### REFERENCES.

- Jour. Amer. Chem. Soc.*, **16**, 809; **17**, 55, 275; **27**, 293; **28**, 648.  
 THIS JOURNAL, **1**, 751.  
 A. W. Dow, "Directions for Using Dow Penetration Machine." Published by Dow and Smith, of New York.  
 A. W. Dow, "The Testing of Bitumens for Paving Purposes." From *Proceedings Amer. Soc. for Testing Materials*, Vol. III, 1903.  
 Byrne, "Inspection of Materials and Workmanship Employed in Construction."  
 Byrne, "Highway Construction."  
 Richardson, "Modern Asphalt Pavements."  
 Stillman, "Engineering Chemistry."  
 Ulzer and Fraenkel, "Chemical Technical Analysis."  
 Thorpe, "Outlines of Industrial Chemistry."  
 Brannat, "Petroleum and Its Products."  
 Sadtler, "Industrial Organic Chemistry."  
 Allen, Vol. II, Pt. 2, "Commercial Organic Analysis."

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### ON THE FORMATION OF CARBENES.

By D. BASIL W. ALEXANDER.

Received March 2, 1910.

Since the appearance of the note on a constant-level reservoir,<sup>1</sup> the writer has received sundry inquiries regarding the last paragraph; it seems therefore advisable to give the investigations that produced that statement. This article is not to be considered exhaustive by any means, but only gives results and hints in the hope that other workers may take up the problem, and give us results that may help to a better understanding of this subject.

As early as May, 1905, it was noticed by the writer that although carbenes in an asphalt are represented by the difference between the amounts soluble in  $\text{CS}_2$  and  $\text{CCl}_4$ , nevertheless when the carbenes are separated and dried, only a portion is then soluble in  $\text{CS}_2$ , showing that a change takes place which renders them insoluble in  $\text{CS}_2$ , and only slightly more so in  $\text{CHCl}_3$ ; this change being brought about either by drying, or some other unconsidered cause, such as the free action of daylight. It is stated by A. S. Cooper, formerly State Mineralogist for California,<sup>2</sup> that by the action of daylight asphalt undergoes polymerization, and certain portions are rendered less easily dissolved than before the action of light. Some work was done along these lines, but was temporarily abandoned on account of other and more pressing business, so it was not until early in 1909 that it was taken up again. At this time it was noticed that certain other laboratories with which the writer had been able to compare results had not agreed with his own results when determining carbenes by Clifford Richardson's carbon tetrachloride method, while other laboratories established and controlled by the writer were in fair agreement. This led to investigation, and it was

<sup>1</sup> *J. Am. Chem. Soc.*, **31**, 1052.

<sup>2</sup> *Bull.* **16**, Cal. State Mining Bureau, p. 18.

found that the chemist consistently finding a larger amount of carbenes than he, was in the habit of standing his solutions of bitumen in  $\text{CCl}_4$  in beakers, on a glass shelf, placed half-way up a window having a northern exposure.

The following experiments were then made: A kettleful of Durango when melted, was thoroughly stirred and portions taken from the top, middle and bottom, and dissolved in  $\text{CS}_2$  and  $\text{CCl}_4$ , then filtered:

	Top. Per cent.	Middle. Per cent.	Bottom. Per cent.
Bitumen by $\text{CS}_2$ .....	99.1	99.3	99.6
Bitumen by $\text{CCl}_4$ .....	94.8	94.4	94.3

Another and larger portion was taken from the same kettle, and from this samples were submitted to several chemists, with the following results:

	Per cent.
Associated results:	
Soluble in carbon tetrachloride.....	94.8
Soluble in carbon tetrachloride.....	95.1
Outside results:	
Insoluble in carbon tetrachloride.....	10.8
Insoluble in carbon tetrachloride.....	11.2
Insoluble in carbon tetrachloride.....	11.9
Insoluble in carbon tetrachloride.....	13.6

From our own sample (which gave 98.9 per cent. soluble in  $\text{CS}_2$ ), two portions, of about a gram each, were covered with 100 cc. of  $\text{CCl}_4$  in an Erlenmeyer flask, one being set on a window ledge and the other in a cupboard in the photographic dark room. These were filtered next day, and amounts soluble obtained:

(a) Exposed in window, 85.3 per cent., or 13.6 per cent. carbenes.

(b) Stood in cupboard, 94.9 per cent., or 4.0 per cent. carbenes.

Showing an increase of 9.6 per cent. carbenes due to the light.

It was considered possible that temperature might have had some effect, so two more fresh portions were covered with 100 cc. of  $\text{CCl}_4$  and both stood together on the window ledge, but one was fitted with a close-fitting sheath of black paper. The results next day were:

(c) Unsheathed flask, 83.7 per cent., or 15.2 per cent. carbenes.

(d) Sheathed flask, 93.8 per cent., or 5.1 per cent. carbenes.

Here we have a difference of 10.1 per cent. carbenes due to light.

The filtrates from these two samples were allowed to stand, both unsheathed, on the regular  $\text{CCl}_4$  shelf in the analysis room in subdued light for a day, and then filtered:

(e) Filtrate from (c) gave additional carbenes, 0.5 per cent. of original amount taken.

(f) Filtrate from (d) gave additional carbenes, 3.3 per cent. of original amount taken.

This seems to show that the carbenes were contained in the sheathed sample and only needed the light to bring them into evidence.

The filtration was done without any precautions against light, and the filtrates were allowed to stand for three days in the dark and again filtered:

(g) Filtrate from (e) gave additional carbenes, 0.6 per cent. of original amount taken.

(h) Filtrate from (f) gave additional carbenes, 1.6 per cent. of original amount taken.

These carbenes might have been produced during filtration, and probably were, so the filtrates from (g) and (h) were stood in full sunlight for three hours, and on filtering:

(i) Filtrate from (g) gave 2.3 per cent. additional carbenes.

(j) Filtrate from (h) gave 7.9 per cent. additional carbenes.

Thus it may be seen that the total amount of carbenes obtained from the two original samples, (c) and (d), differ to the amount of only 0.7 per cent.

To further investigate the possible effect of temperature the mode of procedure was slightly changed; three samples were taken from the original can of supply, covered with 100 cc. of  $\text{CCl}_4$  in three Erlenmeyer flasks; the flask sheathed in black paper was further covered with white paper, another with white paper only, and the third left uncovered. All three flasks were placed on a board and set in full sunlight for 6 hours, and filtered:

(k) Unsheathed flask, soluble in  $\text{CCl}_4$ , 76.2 per cent., or 22.7 per cent. carbenes.

(l) White paper only, soluble in  $\text{CCl}_4$ , 84.4 per cent., or 14.5 per cent. carbenes.

(m) White and black paper, soluble in  $\text{CCl}_4$ , 93.5 per cent., or 5.4 per cent. carbenes.

Only the filtrate from (m) was saved, and that was set in the dark for two months, and on filtering gave:

(n) Additional carbenes 2.5 per cent. of amount taken for (m).

A further standing for two months, in the dark, of the filtrate from (n) gave:

(o) Additional carbenes 0.4 per cent.; but on allowing the filtrate from (o) to stand in full sunlight for only two hours we obtained:

Additional carbenes 10.4 per cent.

Even at this the total amount of carbenes did not come up to the amount obtained in one setting in the sun, as in (k).

It was considered possible that the effect might not be due entirely to the  $\text{CCl}_4$ , and so a fresh sample of the material was spread as thinly as possible on a piece of glass and exposed to full sunlight for  $7\frac{1}{2}$  hours. About a gram of this was weighed out, and also the same amount of the fresh material, and subjected to the regular operations:

Regular method, soluble in  $\text{CCl}_4$ , 93.4 per cent., or 5.5 per cent. carbenes.

Exposed asphalt, soluble in  $\text{CCl}_4$ , 93.7 per cent., or 5.2 per cent. carbenes.

It is evident the  $\text{CCl}_4$  is partly, at least, responsible for carbenes.

A further examination by fusing some of the carbenes obtained with a fusing mixture showed the presence of chlorine in them, a blank determination with the same chemicals showing none.

Having reached this point, we desired to know the reliability of results formerly obtained, so we used two samples that had been reported thus:

Test No.	Per cent. 10790.	Per cent. 10792.
Bitumen by carbon bisulphide.....	99.5	99.5
Bitumen by carbon tetrachloride.....	99.7	99.5
Penetrometer at 77° F.....	34°	54°

Weighed portions of these two samples were dissolved in 100 cc. of  $\text{CCl}_4$  and allowed to stand for 6 hours in full sunlight and then filtered:

10790 bitumen by  $\text{CCl}_4$ , 89.4 per cent., or 10.1 per cent. carbenes.

10792 bitumen by  $\text{CCl}_4$ , 93.7 per cent., or 5.8 per cent. carbenes.

It was here that the effect of penetration was noticed, as the above results show that the harder asphalt contained the larger amount of carbenes, the other conditions being identical, or nearly so.

Carbenes are generally supposed to be produced by overheating asphaltic oils during their condensation into asphalt, and experiments were conducted along these lines. For this purpose three samples of an asphaltic oil were heated at 400° F. until they came to asphalt:

	Penetrometer.	Sol. in $\text{CCl}_4$ . Per cent.
Sample No. 1.....	51	99.8
Sample No. 2.....	25	99.4
Sample No. 3.....	21	99.5

Fresh portions of these three samples were dissolved in  $\text{CCl}_4$  and exposed to direct sunlight for 6 hours and filtered:

	Per cent.
Sample No. 1.....	98.9
Sample No. 2.....	98.2
Sample No. 3.....	98.9

The filtrates were treated the same way, and gave:

	Per cent.
Sample No. 1.....	97.0
Sample No. 2.....	94.8
Sample No. 3.....	94.1

It is apparent that asphalt made by evaporation at a comparatively low temperature does not suffer the decomposition that produces carbenes, and tends to confirm the theory that they are the result of "cracking" in the stills; but the action of light will still produce them, especially when it is run down to a low penetration.

Three samples of Durango that had been dissolved in  $\text{CS}_2$ , decanted, and the bitumen recovered from solution and heated to 300° F., were examined for their solubility in  $\text{CCl}_4$ , with the following results:

		Before treatment. Per cent.	After treatment. Per cent.
Test No. 10615.	Soluble in $\text{CCl}_4$ .....	99.2	99.4
Test No. 10615	Soluble in $\text{CCl}_4$ .....	99.2	99.4
Test No. 10706.	Soluble in $\text{CCl}_4$ .....	92.3	92.8

It will be noticed that the second sample is a duplicate of the first.

It does not appear that the solubility of an asphalt in  $\text{CCl}_4$  is affected by dissolving it in  $\text{CS}_2$ , and subsequently recovering the bitumen.

Satisfactory results were not obtained from refined Trinidad asphalt, on account of the extremely fine mineral matter, so a sample of the Trinidad asphalt was dissolved in  $\text{CS}_2$ , filtered, and the filtrate swung in a centrifuge, the solvent evaporated, and the residue heated to 300° F., this being the same treatment given to the above samples. Test Nos. 10615 and 10706.

The following results were obtained:

Bitumen by carbon bisulphide, 99.7 per cent.

(a) Soluble in  $\text{CCl}_4$  after exposure to sunlight for 15½ hours, 73.9 per cent., or 25.8 per cent. carbenes.

(b) Same as (a) except flask sheathed in white over black paper, 99.3 per cent., or 0.4 per cent. carbenes.

(c) Filtrate from (a) after 6 months in subdued light, carbenes, 2.5 per cent.

(d) Filtrate from (b) after 6 months in cupboard, carbenes, 0.5 per cent.

Filtrate from (c) after sunlight for 7½ hours, carbenes, 4.0 per cent.

Filtrate from (d) after sunlight for 7½ hours, carbenes, 17.0 per cent.

These results appear to subvert the "formation by cracking" theory, and narrow the question down to one of penetration and actinic light. To verify the latter, two fresh portions of the bitumen extracted from Trinidad refined asphalt were dissolved as usual in 100 cc. of  $\text{CCl}_4$ , and the flasks put in two tin boxes, made for the purpose, having one side, respectively, of red and blue glass; these were exposed to full sunlight for 15½ hours and watched so that the sun's rays fell on the solutions through the glass at all times; filtered:

(a) Exposed to red rays gave carbenes, 0.8 per cent.

(b) Exposed to blue rays gave carbenes, 16.6 per cent.

In the case of (b) the flask, after exposure, was stained by the solution on the side next to the light to a dull brown, but hardly stained on the opposite side at all; it was nearly all removed by  $\text{CCl}_4$  with a feather; the flask (a) was not stained, and washed clean. The filtration of these samples was done in the dark room under red light, and there the filtrates were allowed to stand in their respective colored boxes for six months nearly, when they were again filtered in the dark room:



(c) Filtrate from (a), additional carbenes, 0.8 per cent. of original amount taken.

(d) Filtrate from (b), additional carbenes, 3.2 per cent. of original amount taken.

The filtrates were exposed to sunlight for 7 hours and filtered:

(e) Filtrate from (c), additional carbenes, 15.9 per cent. of original amount taken.

(f) Filtrate from (d), additional carbenes, 6.7 per cent. of original amount taken.

The filtrates were again exposed to sunlight for 7 hours, but the sun was obscured nearly all the time; filtered:

Filtrate from (e), additional carbenes, 2.4 per cent. of original amount taken.

Filtrate from (f), additional carbenes, 2.0 per cent. of original amount taken.

These results cannot be called satisfactory, inasmuch as the total amount of carbenes in each case are not the same, as one would logically expect them to be. However, more work will be done on these lines.

It has been noted above that a sample of asphalt showing no carbenes by our regular method, would display them is exposed to light; and it was wondered if the reverse would be true, so a sample that showed 82.2 per cent. soluble in  $\text{CCl}_4$ , though the penetration was  $81^\circ$  Penr., was dissolved in 100 cc. of  $\text{CCl}_4$  and allowed to stand for the regular time of 18 hours, all operations, after weighing, being conducted in the dark room. After filtering in the dark we obtained:

Soluble in  $\text{CCl}_4$ , 92.8 per cent.

So even light cannot produce carbenes unless the conditions are favorable. Investigation along these lines were discontinued for the present, but continuing the subject of penetration, experiments were conducted on Gilsonite, using 100 cc. of  $\text{CS}_2$  and  $\text{CCl}_4$ , and exposing to full sunlight for 7 hours:

	Sol. in $\text{CS}_2$	Sol. in $\text{CCl}_4$
(a) Screened from light.....	99.9	99.6
(b) Unscreened from light.....	99.9	48.0

The filtrates from the  $\text{CS}_2$  solutions were further exposed under the same conditions for 20 hours, but there was no change, except that the flask above the solution was stained brown. The filtrate from  $\text{CCl}_4$  solution (a) was exposed to full sunlight for 7 hours and filtered:

	Per cent
Soluble in $\text{CCl}_4$ .....	76.7

The carbenes in these cases appear gelatinous, and apparently quite different from the carbenes from Durango grade of asphalt; this quality makes them very hard to filter. During the process of investigation of this material, carbenes of a brown color were obtained, but these results are not yet ready for publication.

Some observations relating to the  $\text{CCl}_4$  used may

be of interest, and lead to results throwing more light on this subject. During the distillation of solutions of bitumen in  $\text{CCl}_4$ , to recover the solvent, it has been noticed that  $\text{HCl}$  is evolved if water is present, the residue in the flask becomes quite brittle when the solvent is evaporated, and the sides of the flask used for distillation show the characteristic "carbene ring." The evolution of  $\text{HCl}$  is more marked when a copper still is used. A piece of blue litmus paper suspended over a solution of bitumen in  $\text{CCl}_4$ , especially when in the sunlight, is quickly reddened; again, if a sample of the  $\text{CCl}_4$  itself is exposed for a length of time in a stoppered bottle to sunlight, it will separate into two layers, the upper one about 1 per cent., yellowish, watery, and acid; and blue litmus paper is reddened. This layer, however, is not  $\text{HCl}$ , as it gives a buff, flocculent, not curdy, precipitate with silver nitrate.

#### SUMMARY AND CONCLUSIONS.

It cannot be affirmed that carbenes are altogether formed during the production of asphalt from petroleum in a still, but that they are due:

(1) To a concentration, or hardness, produced under circumstances about which we can only theorize until we acquire greater knowledge; and,

(2) To a condition effected in the asphalt which when a suitable agent (in this case chlorine) is introduced, renders by combination a portion insoluble and brittle; the action is probably analogous to the formation of "acid sludge" in the refining of distillates by sulphuric acid; and,

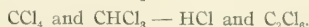
(3) To the action of actinic light on solutions of bitumen in carbon tetrachloride, or on the tetrachloride itself, when chlorine is liberated, and is taken up by the unsaturated hydrocarbons forming an insoluble combination.

#### LATER NOTE.

We are glad to see from Mr. Mackenzie's excellent article in the April number of *THIS JOURNAL* that he has been able to verify in a great measure our own results, and hope that this publicity may lead to some method of knowing and determining accurately these vexatious carbenes.

We would like to further state that following a suggestion of Mr. Ralph Martin it is now our practice to filter our re-distilled  $\text{CCl}_4$  through a layer of  $\text{CaCl}_2$ , which seems to sweeten it considerably.

Another hint we have recently received from Mr. E. O. Heinrich, City Chemist of Tacoma, Wash., is that the formation of  $\text{HCl}$  is possibly due to the presence of  $\text{CHCl}_3$  in the  $\text{CCl}_4$ , derived during manufacture,<sup>1</sup> a reaction being set up under the influence of sunlight, in accordance with the equation:



1000 DATE ST., LOS ANGELES, CAL.  
Feb. 24, 1910.

<sup>1</sup> Richter's *Org. Chem.*, Vol. 1, p. 386.

## THE HYGIENE OF THE SMALL CHEMICAL LABORATORY.

By EDWARD KELLER.

Received February 23, 1910.

In perusing the literature on factory-practice of recent years, one is struck by the widespread tendency, expressed therein, to improve the environment of the working people in all fields of industry. Yet, it is too well known that this problem had been neglected for generations. The chemical laboratories have retained, on the whole and in contrast with the modern industrial plants, much of their mediaeval aspect; they generally are full of dense fumes and noisome odors. Consequently, it may be asserted that the chemist may be made a better paying individual by establishing for him favorable and agreeable surroundings where these do not pre-exist; even though one making such an assertion be suspected of humanitarian motives, for the reasons that he him-

plants and buildings. Any one interested therein may be referred to an article on that subject by P. R. Morse.<sup>1</sup> The discussion will be confined to ventilation by natural forces which, when properly conducted, will be shown to be more efficient than the often defectively installed mechanical means in small establishments.

At first sight this subject-matter might appear almost too trivial for a treatise, were it not for the fact that complaints of the working chemists are universally to the effect, that under certain conditions, of wind or weather the hoods return the fumes into the working room. These facts at once lead to the conclusion of faulty arrangements in the system of ventilation, incidental to the neglect of applying some of the elementary laws of physics by our architects.

Before analyzing the forces which we must utilize or eliminate in the most economic application of natural ventilation, we must recall to mind the dis-

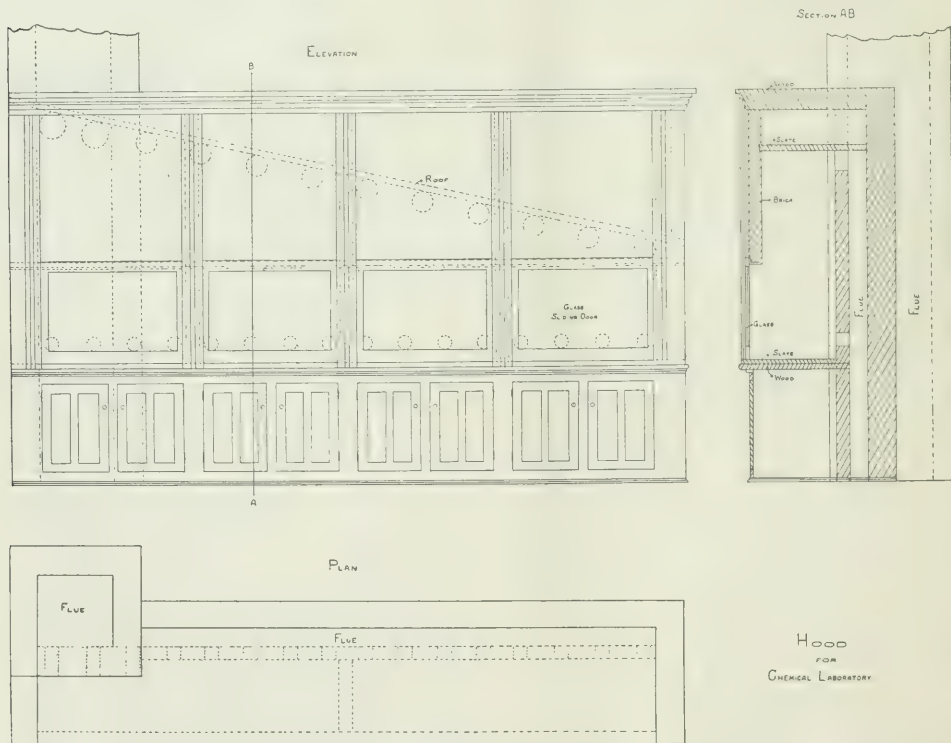


Plate I.

self spends a large part of his life in the chemical laboratory.

*I. Ventilation.*—It is not the purpose of this paper to deal with the latest improved ventilating and tempering machinery installed in some of our giant

advantage of a laboratory ventilating stack, as regards draught, as compared to the stack of a heating plant, due to the former's small difference of temperature within and without. It is for this reason that

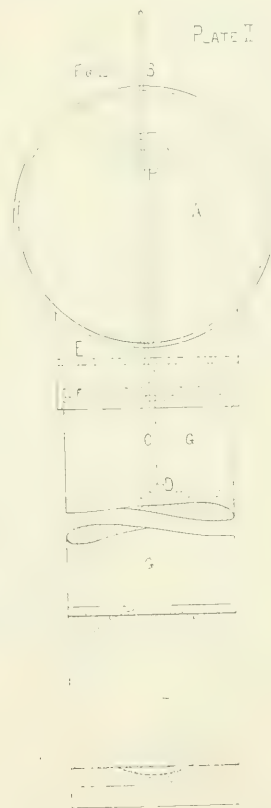
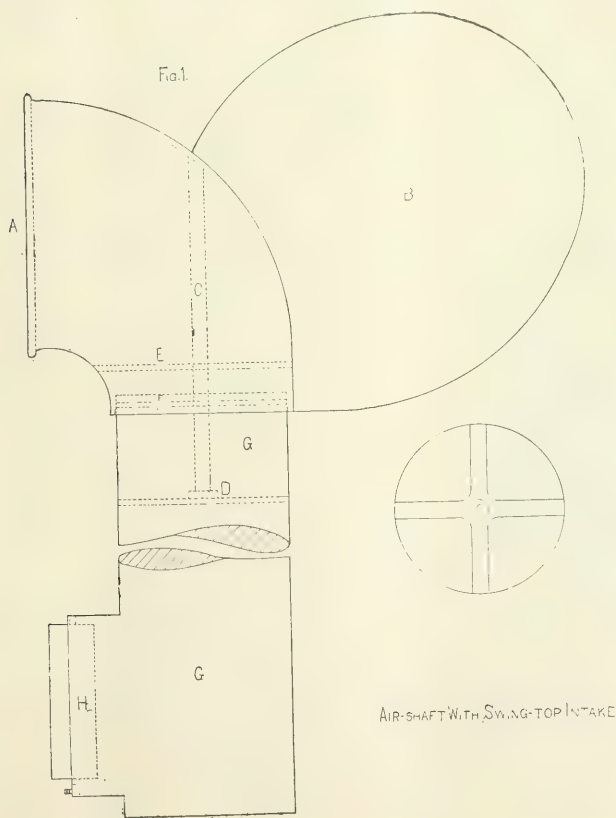
<sup>1</sup> *Engineering Magazine*, February, 1908.

wind and weather play such an important part in its operation. If a certain wind blows down through the stack and drives the fumes from the hood into the laboratory it is not because either east, west, north, or south wind has the tendency to turn at right angles downward. The wind, like any other body in motion, will pursue a straight course, unless deflected by some other force. It has the peculiarity, by blowing over an opening of an enclosed space, to exercise suction or to create within that enclosed space a partial vacuum, while by its velocity-impact it creates a pressure which increases with approximately the square of the wind-velocity. It now becomes self-evident that where the described troubles exist, the stack is offering to the wind a course of least resistance, which again can be due only to a lower atmospheric pressure inside than out, *i. e.*, a partial vacuum existing in the stack and the adjoining room, caused by the suction of the wind in blowing over an open door or window of the respective room. For brevity's sake, the impact-pressure of the wind may be called the plus-pressure: while

the vacuum pressure must accordingly be termed minus-pressure.

It so happens that very few laboratories, or for that matter any rooms, are exposed to the winds in all directions of the compass. Therefore, when the wind blows from the direction of the sheltered or protected side and there are open doors or windows on the opposite side, there naturally results minus-pressure in the room, with consequent backdraught in hood and stack. It thus becomes clear that in order to obtain reliable ventilation, with constant plus-pressure in a room, we must permanently engage the force of the winds by arranging our ventilators in such a manner that at all times there will be an air receiver in the wind direction, or to have what is known as an injector.

In the writer's laboratory building, skylights have been placed in the four main directions of the compass, two of which open directly into the laboratory, while the other two are connected over the ceiling of other rooms. They can handily be raised and lowered from the laboratory and they have the ad-





vantage over the ordinary windows in that the draught from them is less perceptible by delicate people and that it less disturbs the gas flames on the working tables.

Where windows or skylights on all sides of a room are impossible, the difficulty of introducing the plus-pressure, at all times and automatically, may be overcome by a device as shown in Plate II, Fig. 1 an "injector."<sup>1</sup> According to the size of the room, one or more airshafts or pipes, *S*, may lead from the roof or through the side-walls into it. These shafts or pipes are capped with swingtops, having a funnel-shaped mouth, *A*, and a vane, *B*, which keeps the mouth turned towards the wind. The ingress of the air into the room may be regulated by one or more registers *H*.

This principle of ventilating by the wind-pressure is generally carried out on all kinds of maritime vessels, although not by automatic injector swingtops, and it is surprising that architects should not have made more general use of it in buildings where perfect sanitation is a prime requisite. The principle of suction by the wind is found more frequently applied, as is noticeable by the suction swingtops on chimneys, and other forms of "ejectors" on the roofs of buildings and railway cars.

Naturally, the most efficient method for displacing the air in a room is by a combination of the pressure and suction principles. As to the choice between the two, it will hereafter be demonstrated that the former is from four to seven times as efficient as the latter.

The proper principles for the natural ventilation of the chemical laboratory demonstrated and established, it merely becomes a question of hood-capacity to obtain a perfectly sanitary atmosphere. Plate II, Fig. 2, shows the design of a hood from which, with a little attentive regulation of plus-pressure in the room, there is never the slightest issue of fumes or odors. The essential features of this hood are, a double wall in the back with six inches of free space between them; the free space directly connected by its full transverse section with a stack of 4 ft.<sup>2</sup> inner cross section and 25 ft. height, therefore no entry of dust into the hood from this side; openings, or vents, along the slanting roof-line and along the table-line, connecting the hood with the free space between the rear walls and with the stack. Especial attention may be called to these two rows of vents, as the arrangement permits heavy fumes to enter the flue at the base, where the force of the draught is the same as along the roof, and as it also appears to prevent whirling motions inside of the hood by which fumes are sometimes cast out through open doors in front. The hood, furthermore, has vertically sliding, balanced doors and two compartments, one of which contains heating

plates, and the other the hydrogen sulphide generator and sufficient space for filtrations or other special work.

Any heating apparatus in the hood will aid the draught in the stack. In some laboratories one finds, for that reason, a gas flame placed in the latter.

In order to prove the superior efficiency of wind-pressure over such small heating appliances, as just mentioned, for the creation of draught, Table I has been compiled. It shows a comparison of pressures by wind-velocity and the same pressures caused by internal and external temperature differences in stacks of various heights. The left-hand portion of the table, showing definitions of winds, their velocities and corresponding pressures, is taken from "Compressed Air and Its Applications," by Gardner D. Hiscox, New York, 1901. The right-hand portion of the table, having in common the pressure column with the left, shows the temperatures which are necessary, in stacks of 25, 50 and 100 feet heights, to produce pressures equal to those produced by the winds. These temperatures have been calculated by the writer according to the following factors and the deduced formula:

$w$  = weight of external air column at 70° F., normal barometer and height of stack.

$w_n$  = weight of internal air column.

$p$  = wind-pressure; pounds per square foot.

$\alpha$  = coefficient of expansion of gases for 1° F., (assumed to be constant).

$t_a$  = external temperature, arbitrarily taken at 70° F.

$t_n$  = temperature difference between internal and external air columns.

$t_x$  = temperature sought.

$$w - w_n = p; \left( w_n = \frac{w}{1 + \alpha t_n} \right);$$

$$w - \frac{w}{1 + \alpha t_n} = p;$$

$$t_n = \frac{p}{\alpha(w - p)}; (t_n - t_a - t_x);$$

$$t_x = t_a - \frac{p}{\alpha(w - p)}.$$

When  $w = p$ , or  $w - p = 0$ , we have the theoretical maximum of natural draught; then  $t_x = \infty$ .

None of the foregoing figures express directly the amount or strength of the draught, which is simply a function of the air pressure at the base of the stack, regardless of the origin of this pressure. From the wind velocities in Table I we may, therefore, draw direct conclusions as to the draught caused by temperature differences which show identical pressures with the wind velocities. There being comparatively little friction in hood and stack to overcome by the air current, it appears safe to assume that 50 per cent. of the wind-velocity is converted into draught,

<sup>1</sup> This note, subsequently discovered that this principle, and various mechanisms pertaining thereto, were much patented some twenty years ago.

and taking as an example, from our Table I, the case of a strong breeze with 880 ft. velocity per minute, the draught in the stack would be 440 ft. per minute, or the volume of air passing through our stack during the working day of 10 hours would be 1,056,000 ft.<sup>3</sup> To obtain the same draught by heating the air in our 25 ft. stack, an increase of temperature of (251.56-70) 181.56° F. would need be maintained in the stack.

TABLE I.—COMPARISON OF WIND PRESSURES WITH CORRESPONDING PRESSURES CAUSED BY DIFFERENCE OF TEMPERATURE IN STACKS OF VARIOUS HEIGHTS.

Observed character of the wind.	Velocity				Temperature and height of air column. Degrees Fahrenheit		
	Miles per hour.	Feet per minutes.	Feet per seconds.	Pressure per square foot.	25 ft.	50 ft.	100 ft.
Barely observed....	1	88	1.47	0.005	71.32	70.66	70.33
Just perceptible....	2	176	2.93	0.020	75.31	72.64	71.32
Very light.....	3	264	4.40	0.045	82.11	75.98	72.97
Light breeze.....	4	352	5.87	0.081	92.23	80.87	75.38
Fair breeze.....	5	440	7.33	0.126	105.48	87.12	78.41
Very fair breeze...	6	528	8.80	0.181	122.62	94.97	82.18
	7	616	10.27	0.247	144.72	104.72	86.77
Fresh breeze.....	8	704	11.73	0.323	172.49	116.41	92.16
	9	792	13.20	0.408	206.97	130.12	98.33
Strong breeze.....	10	880	14.67	0.505	251.56	146.64	105.55
	11	968	16.13	0.610	307.53	165.67	113.60
	12	1056	17.60	0.726	381.28	188.24	122.78
	13	1144	19.07	0.852	480.36	214.80	133.11
	14	1296	20.53	0.988	618.95	246.20	144.72
Stiff breeze.....	15	1320	22.00	1.135	826.15	283.79	157.82
	16	1408	23.48	1.291	1160.43	328.62	172.40
	17	1496	24.93	1.458	1796.45	383.38	188.84
	18	1584	26.40	1.634	3426.68	450.47	207.19
	19	1672	27.86	1.821	7173.94	535.18	227.93
	20	1760	29.33	2.018	.....	644.24	251.31
Very brisk.....	25	2200	36.67	3.155	.....	2692.07	427.75
High wind.....	30	2640	44.00	4.547	.....	.....	829.12
	35	3080	51.33	6.194	.....	.....	2414.17
Very high wind...	40	3520	58.67	8.099	.....	.....	.....
Gale.....	45	3960	66.00	10.260	.....	.....	.....
Storm.....	50	4400	73.33	12.684	.....	.....	.....
Great storm.....	60	5280	88.00	18.310	.....	.....	.....
Hurricane.....	80	7040	117.30	32.800	.....	.....	.....
Tornado.....	90	7920	132.00	40.500	.....	.....	(1000 ft.)
	100	8800	146.60	50.000	.....	.....	987.16

It may here be pointed out that the draught depending on temperature is also a function of the height of the stack, while the draught caused by wind-pressure is entirely independent thereof. Consequently, in the latter case, the stack may be built as low as you please, while its cross section may be enlarged to such an extent that any desired volume of gases will pass through it.

Plate III shows the apparatus by means of which the relations between plus- and minus-pressure were

determined.<sup>1</sup> For equal pressures at *c*, the corresponding plus-pressure at *a* and the minus-pressure at *b* could be read at the gauges. The latter, used for pressures below one inch of water-column, were of the differential type, capable of convenient reading to one-hundredth of an inch. For higher pressures the ordinary siphon gauge was employed. The results of the measurements are given in Table II.

TABLE II.—COMPARISON OF PLUS- AND MINUS-PRESSURE CAUSED BY WIND OR BLAST OF EQUAL VELOCITY.

Plus or velocity-pressure. Pounds per square foot.	Minus or vacuum-pressure. Pounds per square foot.	Ratio of pressure. Plus to minus.
0.286	0.052	1 : 0.182
0.351	0.078	1 : 0.141
0.806	0.130	1 : 0.161
1.066	0.166	1 : 0.156
1.301	0.239	1 : 0.184
1.545	0.312	1 : 0.202
1.758	0.364	1 : 0.207
2.039	0.437	1 : 0.214
2.341	0.489	1 : 0.209
2.669	0.650	1 : 0.244
4.333	0.962	1 : 0.224
5.894	1.274	1 : 0.216
7.975	1.623	1 : 0.204
9.712	1.956	1 : 0.201
11.616	2.330	1 : 0.201
13.177	2.658	1 : 0.202
14.914	2.939	1 : 0.197
16.646	3.340	1 : 0.201
18.727	3.527	1 : 0.188
19.508	3.886	1 : 0.199

the ratio column it will be noticed that the minus-pressure begins with a minimum and that it reaches a maximum with a plus-pressure of 2.6 pounds per square foot. The figures show the low efficiency of the minus-pressure to be about one-seventh of that of the plus-pressure, while the high one is one-fourth, thus showing the degree of superior efficiency of injectors over ejectors in displacing air in a room.

By comparing the minus-pressure column of Table II with the pressure and temperature columns of Table I, an approximate estimate may be obtained of the damage to the draught in a stack by wind suction, when the latter acts in the opposite direction of the draught. The suction effect of the wind upon a building must, however, naturally be less than that indicated in the ratio column of Table II, for the reason that this effect is active only along the roof- and side-lines, while it is *nil* along the base-line.

**II. Deodorization.**—To render the fumes and odors from a chemical laboratory harmless to the exterior surroundings, it generally suffices to dilute them to a considerable degree with the atmospheric air, accomplished by conducting them through stacks to a reasonable height above the dwellings of the vicinity.

With an efficient ventilating system, such as has been described, and with precautions taken that evaporations of acids, the filtration of malodorous liquids, and the generation of hydrogen sulphide be performed in the hoods, the atmosphere in the laboratory should remain free of all nuisances. Much,

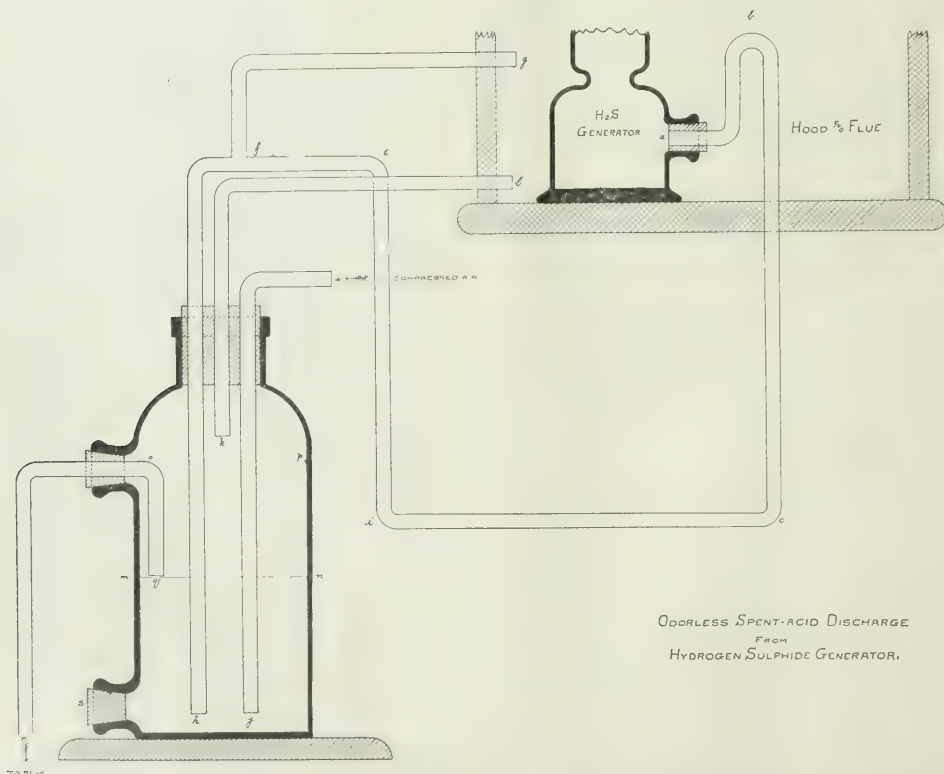
<sup>1</sup> More authoritative data probably exist in the engineering literature. In books available to the writer, they could not be found. For the sake of illustration, merely, actual determinations appeared more simple than the consultation of distant libraries.

of course, depends in the maintenance of discipline by those in charge, and that would appear to be most efficaciously introduced by demonstrating, to the working force's conviction, the utility and efficiency of the contrivances, rather than by adorning the walls with vigorous printed rules.

*Odorless Hydrogen Sulphide Generator Drain.*—There is, however, another difficulty to overcome in connection with the operation of the hydrogen sulphide generator; it is the discharge and disposal of the spent acid. The latter, upon its release from the generator, is surcharged with the gas which it profusely emits, and when left to flow into drains, which have openings into the laboratory, the gas will enter and may not only become a source of annoyance to the men, but may affect the accuracy of certain chemical work and wreak injury to some of the structural materials; or if after leaving the laboratory, this liquor enters open gutters or partially covered sewers, it will vitiate the atmosphere of the neighborhood.

In the device shown in Plate IV, the writer has found a perfect method for eliminating these troubles, it having been in successful operation in his laboratory for about five years. The form of the hy-

drogen sulphide generator is immaterial and therefore only its lower portion, with the drain-tube, is indicated in the figure. It is, of course, placed in a hood. The drain system has a trap, *a, c, d, e*, and a vent at *f*, connected with the hood at *g*. The trap is necessary to prevent the gas from escaping through this duct from the generator, and the vent is required to keep the trap filled with the liquor which, otherwise, would be siphoned out by that part of the drain-tube designated by *e, h*. The liquor thus flows continuously into the reservoir, *R*, at *h*, filling it to the level *o, p*. At this point the discharge tube, *q, r*, is filled and through it the liquor is siphoned off until its level in the reservoir reaches *m, n*, which operation repeats itself automatically. There always remains a stock of liquor in the reservoir whose surface fluctuates rhythmically between the levels *m, n*, and *o, p*. Air is injected into the liquor through *i, j*, and escapes into the hood through *k, l*. At *s* any sediment, or precipitate formed, may be drawn from the reservoir. In addition to the tubes shown in the figure and running through the stopper into the reservoir, a long-tubed funnel may be added, so that filtrates containing hydrogen sulphide may be discarded



ODORLESS SPENT-ACID DISCHARGE  
FROM  
HYDROGEN SULPHIDE GENERATOR.



through this drain and made odorless, instead of being poured into the sink with the well-known effects.

The chemical process in the apparatus is as follows: "The liquor is an aqueous solution of ferrous chloride, surcharged with hydrogen sulphide gas. The injected air oxidizes the ferrous to the ferric salt, which is partially precipitated in a basic form. The ferric chloride in solution, by the intimate contact with the inflowing, dissolved hydrogen sulphide, immediately causes the latter's oxidation and decomposition. In the reaction the ferric salt is again reduced to the ferrous state, while hydrogen chloride is formed, and sulphur liberated:  $\text{Fe}_2\text{Cl}_6 + \text{H}_2\text{S} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$ ."

Owing to the permanent stock of ferric chloride solution in the reservoir the discharge at *r* is always odorless; so is also the air issuing at *l*; the only place of odor emission from the drain-system being at *g*, therefore, its connection with the hood is essential.

For common laboratory use the reservoir need not be of the given design. An ordinary five- or ten-pound, wide-necked bottle will serve the purpose just as well. In this case the siphon-tube *g, r*, is taken through the sealed stopper with the other tubes, and the bottle freed of the sediment, whenever necessary, by disconnecting the stopper and emptying the whole contents.

This device, when constructed of other acid-proof materials on a larger scale, may readily be applied in industrial plants in which hydrogen sulphide is used.

In conclusion, it may not be amiss to call attention to the facts that the extra cost of installation of the improvements is trifling and the operating expenses practically *nil*, while they greatly contribute to the increase of the "joys" of the laboratory.

Acknowledgment is due my assistants, Messrs. Ferrel and McComas, for the preparation of the drawings from which the cuts in this paper were made.

PERTH AMBOY, N. J.,  
Feb. 24, 1909.

## THE CRUCIBLE ASSAY OF PYRITIC CONCENTRATES FOR SILVER AND GOLD.

By GEORGE BORROWMAN.

Received March 22, 1910.

In evaluating pyritic gold and silver ores containing little or no gangue material, the assayer has recourse to three crucible methods. He may remove the sulphur by preliminary roasting; he may lessen the reducing power by using potassium nitrate, or desulphurize by employing iron as wire or nails. The literature affords various criticisms, favorable and adverse, on at least two of the procedures. Mr. R. W. Lodge, in his "Notes on Assaying," states the belief that loss of silver occurs in certain ores due to

the use of niter. He adduces, however, the results of but two fusions. Messrs. Ricketts and Miller, in their text-book on "Assaying," express lack of confidence in the iron method on ore containing much sulphur. No further comment is made. Mr. H. van F. Furman, in his "Manual of Practical Assaying," says the iron method is preferred by most assayers. Again some authorities recommend a charge for the iron method that yields a basic slag, notwithstanding the well-known fact that such slag is likely to carry values. Others, evidently in recognition of this, prefer a charge containing considerably more acid fluxes and some potassium nitrate. Experimental evidence, however, to substantiate the various opinions, is very meagre and on some points entirely lacking. The circumstances lead the writer to make some investigations, in the hope of obtaining definite data as to the relative efficiency of the various treatments.

In all of the work 0.5 A. T. ton of ore, passed through 100-mesh sieve, was taken for each charge. The fusions were made in a gas muffle, excepting those of a few slags, which were carried on in a crucible furnace. The fusions were started at low heat and gradually raised to about 1200° C., the charges being in the furnace about forty-five minutes. Morganite cupels were used. The fluxes, time of fusion, size of buttons, in short all conditions were kept as nearly uniform as possible. The litharge used contained silver, for which corrections were made.

For the first work a Leadville, Colorado, pyrite was selected. It was almost pure iron sulphide, carrying a little copper. The reducing power was 9.1. Three series of four charges were made up. Series No. 1 consisted of assays for the potassium nitrate method, the following charges being used:

Ore.	0.5 A. T. Grams.
$\text{NaHCO}_3$ .....	15.0
$\text{PbO}$ .....	175.0
$\text{SiO}_2$ .....	15.0
Borax glass.....	10.0
$\text{KNO}_3$ .....	28.5
Salt cover.....	...

Series No. 2 was first dead roasted and then fluxed as follows:

Ore.	0.5 A. T. Grams.
$\text{NaHCO}_3$ .....	15.0
$\text{PbO}$ .....	110.0
$\text{SiO}_2$ .....	5.0
Borax glass.....	10.0
Argols (R. P. = 10).....	2.5
Salt cover.....	...

Series No. 3 was made up according to the general type of charge usually recommended for the iron method:

Ore.	0.5 A. T. Grams.
$\text{NaHCO}_3$ .....	30.0
$\text{PbO}$ .....	23.0
Borax glass.....	10.0
4 Iron nails (20-penny).....	...
Salt cover.....	...

The slags in all cases were liquid and poured well. All were glassy excepting those of No. 3, which were basic. No matte formed in any case. Cupellation gave the following results:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
9.01	8.87	7.88
8.90	8.91	7.23
8.95	8.59	8.29
8.95	9.10	8.29
Av. 8.95	8.86	8.05

It will be seen that Nos. 1 and 2 check closely, while No. 3 is uniformly low. The slags of No. 3 being basic were assayed and found to carry on the average 0.91 mg. With this correction, No. 3 checks the others closely.

The same ore was then assayed with the following charge, recommended by Furman:

Ore.	0.5 A. T. Grams.
NaHCO <sub>3</sub> .....	35
PbO.....	20
SiO <sub>2</sub> .....	15
KNiO <sub>3</sub> .....	5
3 Nails (20-penny).....	..
Borax glass cover.....	..

Two fusions were made; the slags were glassy and no matte formed.

Two more charges were run, omitting the nitrate, considerable matte forming in both cases. The two matte-free buttons yielded the following:

	Au + Ag. Mgs.
No. 1.....	9.17
No. 2.....	9.04
Average.....	9.10

These results, it will be noted, are a trifle higher than obtained by any method previously. Furman's charge was further tested by comparing results obtained from it with those from a charge similar to the one used in the first iron fusions. It was taken from one of the recent text-books and consisted of the following:

Ore.	0.5 A. T. Grams.
NaHCO <sub>3</sub> .....	30
PbO.....	20
SiO <sub>2</sub> .....	3
4 Nails (20-penny).....	..
Borax glass cover.....	..

Four charges of each were fused. The slags from the latter mixture were basic, the others as before, glassy. The results of cupellation follow, No. 1 being from the nail-niter treatment:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.
13.61	13.04
13.64	13.27
13.54	13.17
13.74	13.36
Av. 13.63	13.21

These results confirm the preceding. The ore used in the last fusions was taken from a different part of the same lot from which the first assays were made, accounting for the different silver value.

The gold in this ore was merely a trace, too small amount to show any detectable variations. The experiments were concluded by repeating the above iron method tests on a higher grade ore containing more gold. This was also practically pure pyrite carrying values in the form of auriferous argentite. Four assays were made each with of the two iron methods described above. As a check, four more were run by the niter process. The following average results were secured: Series No. 1 is from the iron-niter fusions; No. 2 from the non-niter iron method; and No. 3 from the straight niter assay:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
Av. 78.28	76.54	79.08

Two slags from each were assayed and the following amounts recovered:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
3.00	3.62	0.93
2.67	3.50	0.93
Av. 2.83	3.56	0.93

Not more than traces of gold were recovered from the slags.

#### CONCLUSIONS.

From the foregoing data it seems that with pyrite ores, at least, the maximum amount of niter can be used with impunity, that in fact results are, if anything, a little higher by this method. Iron does not thoroughly decompose highly sulphuretted ores though only silver appears to be carried into the slag. The use of considerable silica apparently assists in breaking up the sulphide, the tendency to matte formation being overcome by a little potassium nitrate. The losses, however, even with basic slags are not very large, but it is evident that when greater accuracy is desired, the more troublesome niter method should be used in preference to the convenient "nail" fusion.

As might be expected, the comparisons show the results of the roasting method to be satisfactory, though higher grade ores might suffer a considerable mechanical loss. In fusing roasted ores which had contained argentite, the writer found that considerable silver was carried into the slag, probably due to incomplete breaking up of silver sulphate in the roasting.

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## THE MILLING OF CANE IN SUGAR MANUFACTURE CONTROL APPARATUS.

By G. L. SPENCER.

Received April 1, 1910.

With very few exceptions, cane sugar factories use heavy mills in the extraction of the juice. In very modern plants the milling equipment consists of a crusher and four mills arranged in tandem. Each mill has three rolls so arranged that the cane receives a double crushing in passing through it. The crusher has two corrugated rolls which break the hard stalks and extract a considerable part of the juice from them, preparatory to the milling. The pressure upon the rolls is usually controlled by hydraulic devices, that upon the top roll of a mill seven feet long often exceeding 500 tons. The woody residue or bagasse is usually sprayed with water after leaving each mill, except the last of the series, from which it is conveyed directly to the boiler furnaces. The water dilutes the residual juice in the bagasse and facilitates its removal in the subsequent milling.

The quantity of juice that may be extracted varies with the setting of the mills, the quality of the cane, care in feeding the cane to the mills, and the quantity of water sprayed upon the bagasse. A careful laboratory control is necessary to keep a milling plant operating at its highest efficiency.

The control includes the calculation of extraction numbers based upon the weight and analysis of the cane and juice; the calculation of the percentage of saturation or maceration water, *i. e.*, the water sprayed upon the partly extracted bagasse; the calculation of the dilution number, *i. e.*, the percentage of water required to reduce the density of the undiluted or so-called normal juice to the density of the mixed juices. An efficient control requires special apparatus, some very efficient types of which are described below.

**Juice Sampler.**—The most efficient sampler in the writer's experience is one designed by an engineer of the Calumet Plantation, Louisiana. This instrument (Fig. 1) samples in proportion to the quantity of cane ground. It rarely clogs or fails to operate. The Calumet sampler is shown in section in the illustration. It consists essentially of a plunger with a perforation near one end and so arranged that this perforation is alternately plunged into the stream of juice and withdrawn with a sample. The reciprocating motion is imparted by a crank or eccen-

tric driven by a belt off one of the mill-roll shafts. Fig. 1 is from a working drawing of a sampler arranged to draw juice from the inclined canal or chute from a crusher. The projecting lip, inside the canal, insures the filling of the hole in the plunger. The sample is discharged from the bottom of the plunger into a gutter leading to a storage vessel containing a preservative.

Various modifications of this sampler permit its use in sampling from canals and pipes.

**Juice Scales.**—Automatic scales have been used, usually with indifferent success, in weighing the mill juice. The "hammering" of the heavy charges requires very substantial and expensive construction in an automatic scale and almost constant skilled attention. The hopper- or tank-scale with type registering beam, is inexpensive and efficient. The tanks should be provided with a hot water spraying device to keep them clean.

**Apparatus for Bagasse Analysis.**—Bagasse is necessarily sampled by hand, owing to milling conditions and the nature of the material. It is usually prepared for analysis by cutting with a butcher knife, a knife mounted similarly to the old-fashioned feed cutters, or by chopping devices. An efficient machine is made in Delft, Holland, especially for preparing bagasse for analysis.

The customary quantitative tests are moisture, fiber (marc) and sucrose. The writer has devised the apparatus described below to minimize labor and to reduce the personal errors and especially to

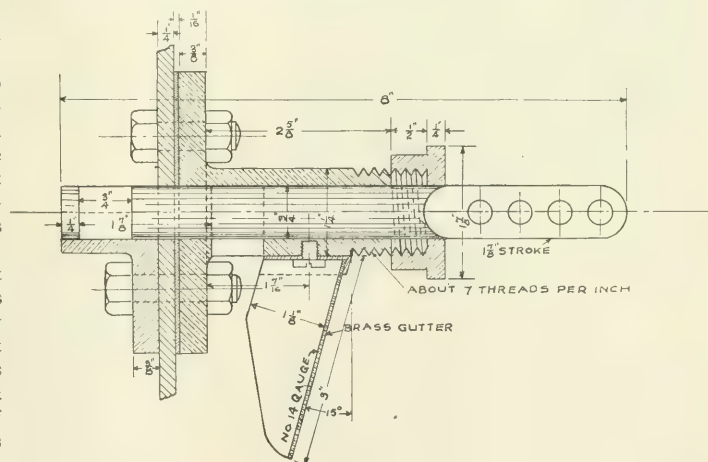


Fig. 1.

enable chemists to promptly obtain the desired data.

The oven shown in Fig. 2,<sup>1</sup> in section, from a working drawing, will dry 200-gram samples in about 90 minutes. Efficient vacuum ovens require from 4 to

<sup>1</sup> Suggested by the Soxhlet oven.





planks, but he has since equipped the laboratories with ovens of cast iron, as per Fig. 2. The oven should be insulated with magnesia covering. It is very essential that all joints be well made and that air enter the oven only at the distributing pipe. The nozzle of the ejector is designed for steam of about 70 lbs. pressure, and for low pressures the opening may be larger than indicated. Failure to obtain the desired temperature, given a good steam pressure, is usually due to leakage of air at the joints or to drawing too little air over the coils.

In the usual method of estimating the sucrose in the bagasse, 50 grams of the material are digested in a flask, at boiling temperature, with 500 grams of water containing 5 cc. of a 5 per cent. solution of carbonate of sodium. The flask is fitted with a reflux condenser. The time consumed in introducing the bagasse into the flask and the errors involved, the large item of breakage and occasional loss of tests, led the writer to prepare special copper apparatus. This apparatus is a copper beaker 4 inches in diameter by 6 inches deep and provided with a flange and ground joint brass cover. The cover should be heavy and have a hole in it to receive a cork and tube condenser. A straight tube about four feet long forms a suitable condenser. A thin metal tube fixed permanently to the cover may be used but glass is more convenient in controlling the temperature. Clamps are only necessary for holding the cover, when the apparatus is placed in an inclined position in a water bath. An electric hot-plate is the most convenient heating device.

It is probable that the new Sachs-LeDocte digesters, but of large size, used in the analysis of sugar beets, would answer in bagasse analysis, especially where a water bath is used in heating. In this apparatus a brass ring cover is used. A thin rubber

vacuum is sufficient to hold the cover in position, providing the contents of the beaker are not heated to boiling. The Sachs-LeDocte apparatus as arranged for use in beet analysis is shown in Fig. 3.

A plain copper beaker with a rubber cap slipped over its edges would answer the purpose in bagasse analysis, though the life of the rubber would probably be short.

CUBAN AMERICAN SUGAR COMPANY,  
NEW YORK AND CUBA.

## AN ELECTRIC COMBUSTION FURNACE, LABORATORY TREATING FURNACE AND RHEOSTAT.

By GEORGE M. BERRY.

Received February 17, 1910.

On account of the increased demands upon an already well loaded gasoline gas generator with the attendant impoverishing of the air in the room, where among about one hundred burners six combustion furnaces were kept going constantly during the day, the cost involved owing to the use of high grade gasoline, and on account of the lack of an assuredly sufficient heat to yield complete combustion, without especial preparation of samples, at times when the gasoline in generator was getting "thin" the writer determined to use some form of furnace heated electrically. Knowing something of the workings, but nothing of the construction of the furnaces used by Mr. C. M. Johnson,<sup>1</sup> and something of the platinum wound furnace described at the May 1908 Meeting of the Iron and Steel Institute, but not feeling satisfied with either of these, the writer, in July, 1908, set about some experiments with a view to making a more satisfactory furnace. A brief summary of the more important steps of the work and a detailed description of the furnace as adopted, together with some salient points concerning the making and materials, are here given.

The first furnace had a 10" x 3" diameter iron cylinder as the outer casing. As the heating element it had a 24" x 3/4" bore quartz tube covered for the middle 11" with asbestos cloth and wound for the middle 7 3/4" at twelve turns to the inch with 22 gauge (B. & S.) nichrome wire, using twenty-seven feet of the wire. The space between the heating wire and the three-inch iron cylinder was filled with chemically pure powdered magnesium oxide. This furnace lasted forty-five ten-hour days. At 115 volts it took 3.5 amperes at first, gradually dropping to 2.4 amperes on the forty-fourth day, and yielded a temperature of about 1750° F., which gradually dropped to about 1450°.

Furnace No. 2 had a 12" x 6" diameter iron cylinder as outer casing. As the heating element a 24" x 3/4" bore quartz tube covered for the middle 13" with asbestos cloth and wound for the middle 7 3/4" with

<sup>1</sup> J. Am. Chem. Soc., 30, 773.

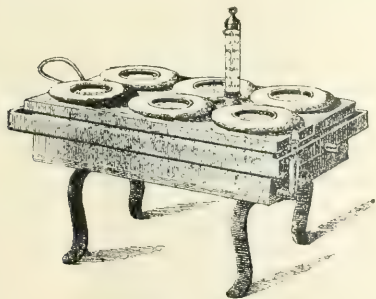


Fig. 3.

cap is slipped over the ring. In placing the cover in position on the beaker, the rubber is bulged downwards by pressure of the thumbs and on releasing it a partial vacuum is formed in the vessel. This

22-gauge chrome nickel resistance wire from another manufacturer, using twenty-seven feet of the wire. The space between the heating wire and the 6" iron cylinder was filled with "light" calcined magnesium oxide, commercial. This lasted fifteen ten-hour days. At 115 volts it took 3.5 amperes, gradually dropping to 2.8 amperes and yielded a temperature of about 1850° F., dropping to 1800° F.

Furnace 2A was made the same as Furnace 2 and with same kind of wire, but with chemically pure MgO as heat insulator. The results were about the same, except for a slightly increased length of life. Furnace 3 was made identical with Furnace 2 except that "heavy" magnesium oxide was used as the heat insulator. This lasted two and one-half hours.

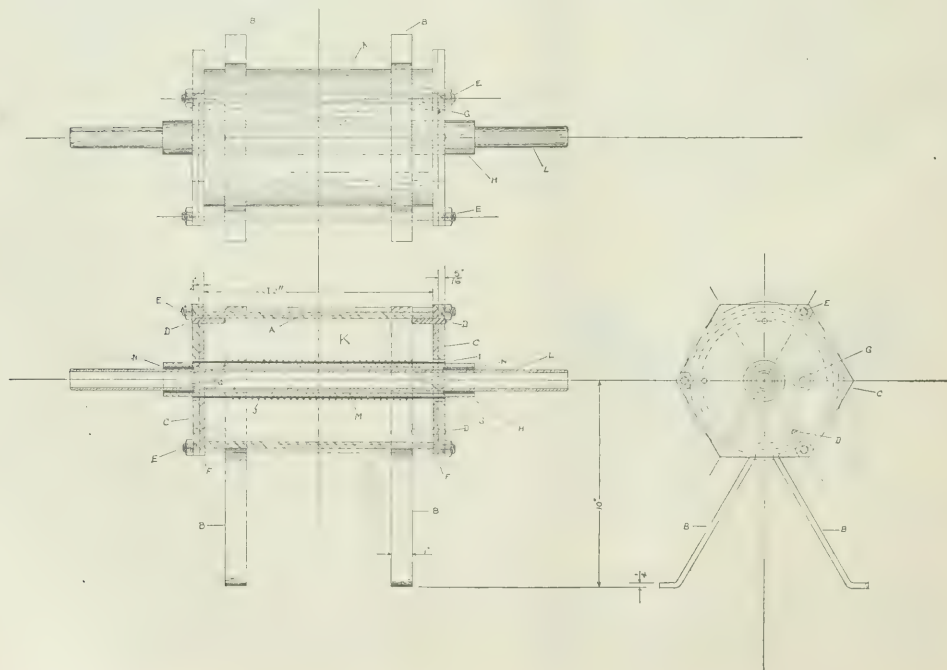
Furnace 3A was made with the outer casing a 12" x 6" diameter iron cylinder. The heating element was a 15" x 1 1/4" bore tube covered with asbestos and wound for 7 3/4" at eight turns to the inch, using about thirty feet of the same kind and size wire as used in No. 2. The space between the heating wire and the six-inch iron cylinder was filled with a double layer of asbestos pipe covering. The space between the 1 1/4" bore tube and the combustion tube was filled with precipitated silica. The life of this furnace was fourteen ten-hour days. At 115 volts it took 4.1 amperes, dropping to 3.2, and yielded a temperature of about 1850° F. Furnace 4 was made iden-

tical with number 3A, except that eight inches was wound at six and one-half turns to the inch, using about twenty-five feet of the same wire. A little shorter life and higher temperature were obtained.

Furnace 5 was identical with Furnace 3A, except that 8 1/8" was wound at eight turns to the inch with 18-gauge (B. & S.) Driver-Harris nichrome wire, using thirty-one feet. The life of this furnace for a fourteen-hour day was exactly four months. At 115 volts it took 4.4 amperes and yielded a temperature of 1920° F.

Furnace 8 was made like 5, except that 7 11/12" was wound at twelve turns to the inch, using forty-five feet of the wire. Chip graphite was used between the two tubes. The life of the furnace here for a fourteen-hour day of constant use was five months and four days. At 112-117 volts it took 3.6 (mean) amperes. The temperature was maintained at 1750° F. to 1850° F. with this current flow. With this furnace it was found that receding from the middle four inches of the heated zone the temperature dropped rather more sharply than is desirable. The temperature being recorded at the middle, 1800° F.; at each end of the middle seven inches, 1590° F. This is corrected in the furnace as adopted by winding for more length of tube

*The Combustion Furnace as Adopted.*—The outer casing consists of a piece of six-inch iron pipe A, 12" long supported by the 1" x 1/4" legs B, which en-





cicle the pipe and are spread at the underside, so that the angle between them is of about sixty degrees. At the bottom the feet are bent outward to the line of the horizontal. The height to the center of the furnace is ten inches. The two heads C, which are alike, are of  $\frac{5}{16}$ " plate cut under the shears to hexagon  $\frac{7}{4}$ " between their parallel edges. They are equipped with three equidistant pins D, on a  $\frac{5}{4}$ " circle. These projected inward, are riveted, are  $\frac{3}{4}$ " long  $\times$   $\frac{1}{4}$ " diameter and serve to prevent the heads falling from the 6" cylinder while the insulators and wires are being adjusted just prior to drawing the two heads together with the bolts. They also serve to hold the heads concentric with the cylinder. The heads are further equipped with five holes, having in the alternate angles  $\frac{3}{4}$ " holes centered on a  $\frac{7}{8}$ " circle. Through these three holes pass the bolts E, which draw the heads together and hold them tightly in place. The joint between the head and the cylinder is made tight by a ring of asbestos board F. The center of the head has a two-inch hole, while at the intersection of the horizontal axis and a  $\frac{3}{2}$ " circle is a  $\frac{3}{4}$ " hole. Through this is placed, with the flange inward,  $\frac{3}{4}$ "  $\times$   $1\frac{1}{2}$ " porcelain insulator G.

The heating element consists of a  $15" \times 1\frac{1}{4}"$  bore quartz tube H, covered for the middle thirteen inches with one layer of "thin woven asbestos cloth" I, and wound with the resistance wire J, so that the windings are tightly imbedded in the asbestos cloth and do not touch each other and so that the ends cannot slip. For the bore given it will be found that the tubes bought in the market will yield an average winding circumference very close to  $5\frac{1}{2}"$ . For the 110 volt circuit approximately fifty feet 18-gauge nichrome wire is used. For the 220 volt circuit the results desired are achieved by simply connecting two furnaces in series. The tube is held in the lathe for winding by an arbor of soft wood which fits the inside of the tube, runs through it, and has projecting end enough to screw a "dog" on to. The asbestos cloth should be cut thirteen inches long by about six inches wide. Then the lengthwise threads are unraveled until the woven piece is about five and one-half inches wide, saving the ravelings for binding. The cloth is held in place around the tube preparatory to winding by tying it at each end and in the middle with some of the threads unraveled from the cloth itself. At about  $2\frac{5}{8}"$  from the end of the tube the wire—which should be on a spool in case the tube is to be hand-wound—is threaded with about  $\frac{3}{4}"$  stitches through the asbestos cloth for one complete turn, and the end is drawn through so that there is a free end about 12" long. This free end is wound around the cloth and made fast to the "dog," which couples the arbor running through the tube with the lathe. The lathe is now started by having a boy pull the belt, or after experience has

been gained by a very low-speed power. The first turn is made to begin at  $2\frac{3}{4}"$  from the end and the winding continued at eleven turns to the inch until  $9\frac{1}{2}"$  have been wound. The wire is held firmly in its place on the tube, while it is cut leaving about seventeen inches free end. This end is threaded with about  $\frac{3}{4}"$  stitches through the cloth for a complete turn as at the beginning, and the end held tight while at both ends the asbestos cloth at the place where the wire is threaded through it is bound and tied with five or six turns of the asbestos thread unraveled from the cloth. This tying of the asbestos string around the tube where the windings cease serves admirably to prevent the loosening of the wire on the tube during subsequent handling. Care should be used at all times to avoid sharp kinks in the resistance wire, as it is likely to break when straightened. The heating element is now ready for the heat insulator.

The heat insulator consist of two pieces—one for  $1\frac{1}{4}"$  pipe, the other for 3" pipe—of magnesia-asbestos pipe covering and some asbestos paper (Kearby and Mattison's "Magnabestos" and Johns-Manville 85 per cent. magnesia pipe coverings have been found highly satisfactory.) Both pieces of the pipe covering are twelve inches long. This is readily cut with any kind of saw. The  $15" \times 1\frac{1}{4}"$  quartz tube, on which is wound the heating wire, is encased with equal projecting ends in the smaller piece of the asbestos pipe covering, which is in turn encased in the larger piece of the same material, so that the joints of the two sizes do not come at the same place. The loose ends of the wire must of course be kept free. The outside of the 3" pipe covering, which has a diameter of about  $5\frac{9}{16}"$  is wrapped with a strip  $12\frac{1}{2}"$  wide of asbestos paper until the diameter of this heat insulating material is 6" and just slips snugly into the 6" iron pipe of the outer casing. When the heating element and the heat insulator have been placed in the 6" iron pipe of the outer casing, the loose ends of the heating wire or lead wires are drawn through the  $\frac{5}{8}"$  porcelain insulators in the hexagon heads. The heads are put in position and drawn tightly to the ends of the 6" iron cylinder by the long bolts.

The furnace is now ready for the combustion tube L, which is inserted through the  $1\frac{1}{4}"$  bore tube. For the middle 12" of the two tubes the space between them is tightly packed with the *Heat Conductor M*, which is chip Ceylon graphite. The graphite is held in place by a ring N, at each end of it, made by wrapping a strip about  $\frac{1}{2}"$  wide of asbestos cloth around the combustion tube. This serves also to hold the two tubes concentric. The graphite can be most easily introduced between the tubes by setting in place one of the asbestos rings, then standing the furnace on end on a tripod with the asbestos ring at the downward end and pouring the graphite

from a sheet of paper into the space between the two tubes, tapping meanwhile on the upward projecting combustion tube. When the graphite has been solidly packed in for the desired twelve inches, the asbestos ring is packed in place at the upper end. It is desirable to have these asbestos rings packed in tightly, so that large amounts of air cannot get into the graphite and effect a gradual combustion of it. The furnace is now completed and ready for connection to the power circuit and rheostat. The connection to the resistance wire is made by coiling tightly around it for ten or twelve turns copper wire of about 18 ga. Connection can be made from this copper wire to any desired conductor.

As winding for the heating element, the nichrome wire from the Driver-Harris Wire Co., Newark, N. J., seemed to give the best results.

The time required for the winding reduces itself, after some experience, to a short and easily executed operation. The writer, with the help of a boy, has repeatedly wound with hand feed, including all manipulations, three elements in an hour.

The life of the element is, of course, effected much by the care exercised in the daily use of the furnace. It is important, for instance, that the element, after it has been in use some time, should not be subjected to any sudden jar or jerk, such as is occasioned when the hand slips off the stopper when tightening it in the combustion tube just after inserting a boat. The element should not be subjected to any undue longitudinal or rotary motion in this operation of corking the tube, as such abuse tends to loosen the element from the heat insulation and also increases the possibility of short circuit of the windings. Four elements used in pairs by the writer and kept under heat for a 14-hour day, each lasted four to five months. He has now been using for about three months his third pair of elements.

Some irregularity has been noted with some lots of wire received, due to its having been heated too hot in the annealing. Such wire shows in the fracture a coarse crystalline structure with a bright lustre at the edge. It is brittle. Extreme care must be taken to avoid short kinks in it and consequent breaking. If too bad it can be annealed by passage of the electric current; or with those inexperienced in this, it should be returned to the makers, to be replaced with wire that is satisfactory.

The furnace to yield 1800 to 1850° F. should have connected in the circuit about 3 to 5 ohms rheostat resistance, depending on the voltage, and should take 3.2 to 4.0 amperes, depending also on the voltage. Where, on account of rather coarse sample, or for other cause, it is thought advisable to temporarily raise the temperature of the furnace above 1800 or 1850° F. this can be done by simply cutting out one or two ohms of the rheostat resistance. How-

ever, some judgment must be used in doing so with a heating element that has been in use some months, as the wire has become somewhat oxidized and is somewhat reduced in cross section area. The temperature may be raised at any time by cutting out some of the rheostat resistance, but with this or any other kind of wire resistance furnace excessive temperature is always at the expense of the life of the furnace.

As heat insulator many materials were used with varying degrees of success. Powdered MgO, C. P., is satisfactory. MgO of the commercial grade both "light" and "heavy" seemed to contain some agent that attacked the heating wire. This objection might be overcome by a thorough ignition of the commercial grade at high temperature before using. Of the various heat insulators tried other than that described in the furnace as adopted for general use, and MgO that which would seem to lend itself under some circumstances to a practical using, is a special form or brick made from fire clay. It is made cylindrical, so as to be, when burned, 12" long by 7" diameter with a two-inch hole through center of its circular cross section. This brick was made both in one piece and in two longitudinal sections. There are objections to this brick arising from the mechanical packing and the handling of the heating element with them, the breaking of the brick, and the lack of suitable equipment in most places for making them. If this form of brick should be used the iron outer casing would not be necessary. Some form of support with cylindrically hollowed top or with upward projecting pins to prevent rolling is all that would be required. However, for reasons of cleanliness and durability, the outer casing as described was adopted and for reasons of cheapness, ease with which obtained, and good results achieved, the pipe covering as described was also adopted.

While this description is given using a quartz tube, the time required for removing the combustion tube and replacing it with another is so short that any other kind of tube—porcelain, glass or platinum—may be put in service in the furnace at will. This changing of combustion tubes when not a necessity is hardly to be recommended, however, with a furnace heating element which has been in continuous service some months. The reason for this is the increased likelihood of short circuit of the turns of wire on the outer quartz tube caused by these turns becoming displaced (the asbestos cloth having shrunk) when this tube is put in the vertical position for introducing the graphite between the two tubes. On account of not being able to use red lead or any oxidizing flux in quartz tubes it is the practice in this laboratory, where carbon in a great number of all the varieties of ferro alloys is required to be determined, to keep a pair of furnaces equipped

with 24" by  $\frac{3}{4}$ " bore Royal Berlin porcelain combustion tubes ready to be connected in circuit for use whenever needed. Of course the usual precautions against breaking a porcelain tube must be observed when introducing the boat into the porcelain tube.

The furnace here given as adopted for general use has proven highly satisfactory for the uses intended. The features embodied in the use of the thin woven asbestos cloth as a bed for the wire windings and the use of the graphite in the space between the tubes as the heat conductor are highly valuable and are, so far as the writer is aware, entirely new. The asbestos cloth can be obtained from any chemical apparatus supply house; the chip Ceylon graphite from any manufacturer of plumbago crucibles.

The actual cost for the entire furnace as made is itemized as follows:

Outer casing:	
Materials.....	\$0.76
Labor.....	2.26
Heating element:	
15" x 1 $\frac{1}{4}$ " bore quartz tube.....	3.12
Asbestos cloth.....	0.15
Wire.....	0.53
Heat insulator.....	0.22
Porcelain insulators.....	0.01
Graphite.....	0.05
Total.....	7.10

It is worthy of note that the only parts that deteriorate so as to need replacing at the time of successive rewindings of the heating element are the asbestos cloth, the resistance wire and the inner piece of pipe covering, with an aggregate cost of ninety cents.

The laboratory treating furnace is used in two sizes. The smaller for the 110 volt circuit is made in two variations. One of these is exactly like the combustion furnace with the omission of the combustion tube. The other is identical except that 17-gauge nichrome wire is substituted, winding 10  $\frac{1}{2}$ " at eleven turns to the inch. Working in temperatures higher than are needed for combustion furnace practice, this larger wire affords an increased length of life over the 18-gauge. The maximum safe carrying capacity as given by the manufacturers is 9 amperes for the 18-gauge and 10 amperes for the 17-gauge. This is doubtless true for the wire in the open air, but when encased in a heat-insulating material 50 to 60 per cent. of these figures should not be exceeded. When either this or the large furnace is in use, each end of the quartz tube is plugged tightly with asbestos wool to hold the heat.

The larger size is for the 220 volt circuit. It is similar to the combustion furnace. The outer casing has an iron cylinder which is 8" inside diameter by 17" long. The heating element is made on an 18" x 1  $\frac{1}{2}$ " bore quartz tube. 18-gauge nichrome wire is used, winding 15  $\frac{1}{2}$ " inches at eleven turns to the inch, using about 90 ft. of the wire including the leads from the furnace. As heat insulator, two layers,

each 1  $\frac{1}{2}$ " thick, of magnesia-asbestos pipe covering of size for 1  $\frac{1}{2}$ " and for 4  $\frac{1}{2}$ " pipe are used.

These furnaces have value in affording a very thoroughly uniform temperature for their full length, except the extreme ends. They have also the advantage of having nothing about them which produces dirt in the laboratory. They cannot be said to be desirable for constant use in temperature approaching the "breaking down" point of the wire. The life of the furnace, when yielding a temperature 2200° F. and above, is short. In some instances, where the conditions afforded by a tube of this type have been desired, a temperature of 2400° F. has been maintained for a short time. The temperature may be raised (within the limits of endurance of the wire) or lowered at will and maintained at any desired temperature by simply cutting out or throwing in resistance with the rheostat. The furnace is found very useful in annealing small pieces of steel for analytical purposes and in handling pieces, where the size will permit, which are preferably treated in the laboratory. It is useful in recalcence determinations and in other experimental work of various sorts where a controllable, constant and uniform temperature in an atmosphere free from the influence of flame is desired.

*The Rheostat.*—During the early stages of experimentation with the furnace the problem of a satisfactory rheostat presented itself. Not being able to find in the market one built for just the conditions at hand, the one here given was designed.

It is made in the form of a spool and consists of a sheet steel or iron cylinder (1), with wood fiber top and bottom ends (2). The spool is held together by four bolts (3), 5  $\frac{3}{8}$ " long by  $\frac{1}{4}$ " diameter, extending completely through the spool just inside the metal cylinder, thus serving to hold the ends in place and to keep the cylinder concentric with the coil-button circle (4). A layer of asbestos cloth or paper (5),  $\frac{1}{16}$ " thick, is wrapped around the cylinder and is held in place by the coil of resistance wire (6). One end of this resistance wire is fastened under binding post (7), which is in the corner of fiber board bottom. The wire is then wound tightly around the cylinder in coils  $\frac{1}{4}$ " apart and the other end fastened under the first screw (8) of the coil button circle. Twenty turns are thus wound on the spool. The sheet metal cylinder, which is 5" long and 4  $\frac{1}{8}$ " outside diameter, is increased to 4  $\frac{1}{4}$ " diameter by the asbestos covering, giving a circumference of 13.35". For the windings 22-ga. (B. & S.) nichrome wire, which has a resistance of 0.9 ohm per foot, is used. A coil of this size has then a resistance of one ohm per turn. The fiber top is provided with a circle of coil-buttons twenty-two in number placed  $\frac{1}{2}$ " apart between centers at a radius of 2  $\frac{5}{8}$ " from the center of the fiber top.



Brass bolts (round-head machine screws) 8 x 32 size and  $7/8$ " long are used for these buttons. Holes the body size of the screws are drilled through the fiber top, the screws inserted, and one nut screwed tightly on the under side, thus holding the bolt. Each turn of the resistance wire is in succession tapped by pinching around it a piece of copper wire (9) about 18-ga., which is led upward to the lower end of the

circuit; placing arm on the next button (18) cuts out one turn of resistance wire (6), giving 19 ohms. Advancing thus each button cuts out 1 ohm. Button (19), which is connected to the first coil above (7) thus gives 1 ohm. Button (21) (not shown in drawing) is adjacent to button (19), connection from this drops directly down, through the bottom fiber board, and is connected to (7). This gives the full load without resistance. Button (20) (also not shown) is adjacent to (8). It is unconnected and breaks the circuit.

The cost of materials of the rheostat as made by the writer, has not in any case exceeded \$1.02. The mechanic's time should not exceed two hours.

The rheostat as first made by the writer had for the top, slate of  $1/2$ " thickness, and had the binding posts adjacent and on the same circle as the coil-buttons. The use of the board fiber and the arrangement of the binding posts as here shown was introduced by Mr. M. A. Allen at the time of his beginning the use of this furnace in May, 1909. The use of the board fiber has, as compared with slate, the decided advantages of being easily procured, easily cut and drilled, and of being non-breakable.

It has been the purpose in this article to give to all fellow laborers the necessary details of the information gleaned, in the hope that it may be of help to some and so that any can, by following the details given, produce at nominal cost a furnace which will do the work for which it was designed.

The writer is indebted to Mr. Myron A. Allen, Chemist to the Brown-Lipe Gear Co., for his very kind service in making the accompanying drawings of the furnace and the rheostat and also for the changes mentioned in the design and material of the rheostat.

LABORATORY OF HALCOMB STEEL COMPANY,  
SYRACUSE, N. Y.  
January, 1910.

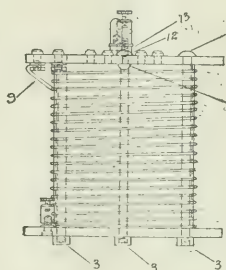
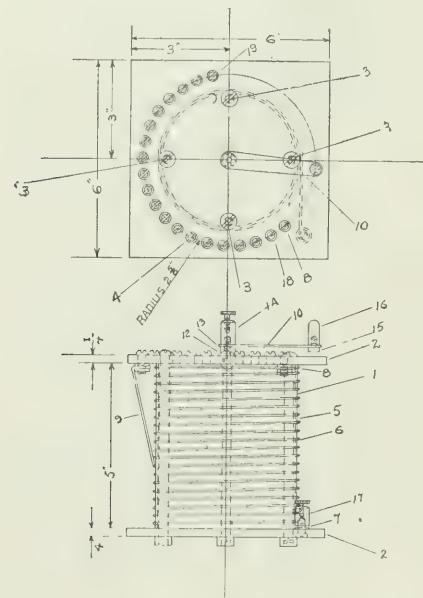
[CONTRIBUTION FROM THE LOUISIANA SUGAR EXPERIMENT STATION, AUDUBON PARK, NEW ORLEANS.]

## OCURRENCE OF FORMALDEHYDE IN SUGAR CANE JUICE AND SUGAR-HOUSE PRODUCTS.

By P. A. YODER AND W. G. TAGGART.

Received April 2, 1910.

In an investigation on some minor constituents of the sugar cane and sugar-house products, we diverged from the main branch of the problem pur-



corresponding brass bolt, where it is bent around the bolt and held against the first nut by a second nut. The switch arm (10) is a piece of sheet brass about  $1/16$ " thick and  $5/8$ " wide, having a hole with about No. 19 drill (0.166" diameter) through each end  $2 5/8$ " between centers. Through the center of the fiber top is a No. 19 hole. Through this hole is inserted from the lower side a No. 8 x 32 brass screw (11). A brass nut (12) is screwed down tightly on the top side and a washer or jamb nut (13) is put on. One end of the brass arm (10) is placed on the bolt over this washer and a binding post (14) is screwed on. The binding post should be tight on the screw (11) and be stationary, but the brass arm (10) should be free to turn. The other end of the arm is provided with a brass screw (15) and a fiber handle (16). The switch arm should, of course, press firmly on the coil-buttons so as to give a good contact. A wire carrying the electric current is inserted at (17), the current passes through the resistance wire (6) and out at (8) through brass arm and to binding post (14), where connection is made to furnace wire. When the arm is on button (8) the entire 20 ohms are in

sued (the acid constituents) to investigate the occurrence of formaldehyde and incidentally for the further elaboration of a method for quantitatively estimating small amounts of formaldehyde. We were led to this sideline investigation by a consideration of the facts (1) that formaldehyde is very convenient to use and frequently is used to preserve fresh juice in the sugar house when boiling is interrupted from any cause; (2) that it is recommended by some as a clarifying agent; (3) that formaldehyde is objectionable in food products; and (4) that it has never, as far as we know, been proved, but is generally assumed that it all boils away in the evaporation of the juice to a massecuite. Further complicating the problem are some recent reports that in caramelizing sugar or even in boiling sugar solutions, formaldehyde is formed. Trillat<sup>1</sup> and A. A. Ramsey<sup>2</sup> report thus. Chas. H. La Wall<sup>3</sup> calls into question the conclusions of Trillat and Ramsay, pronouncing the test which the latter used as unreliable. That formaldehyde can form unstable compounds with some of the sugars has been reported by several investigators. Lippmann<sup>4</sup> mentions such a compound with cane sugar.

The preliminary work on the detection of the formaldehyde in sugar-house products and on the quantitative methods for its estimation was done by us jointly, the junior author carrying out most of the laboratory tests. The working out of final details of the quantitative method used and its application to the juices and sugar-house products reported here was done by the senior author, who alone and in a private capacity is responsible for the formulation of this report and the conclusions drawn.

#### *Methods for Detecting and Estimating Formaldehyde.*

—Of qualitative tests for formaldehyde there is no lack and many of them are exceedingly delicate. The reliable quantitative methods usually mentioned in text-books, *e. g.*, the KCN and AgNO<sub>3</sub> method, or the H<sub>2</sub>O<sub>2</sub> acidimetric method, are not sufficiently delicate to use with the very small quantities with which we found it desirable to work. Hehner's test with milk and concentrated H<sub>2</sub>SO<sub>4</sub> containing a trace of iron, as well as a similar test with HCl, seems to be characteristic of formaldehyde and so delicate for qualitative work that we were led to look hopefully to modifications of these for a quantitative method which, even if not extremely accurate, is sufficiently accurate and delicate for our purposes. F. W. Richardson<sup>5</sup> modified Hehner's method to make it colorimetrically quantitative, using in place of milk a clear solution containing albumose, which he prepared

by incompletely digesting egg albumen with a solution of pepsin and HCl. Seeking a similar substitute for milk in the method with ferruginized concentrated HCl, we tried first a solution of dried peptone, such as is used in bacteriological laboratories. This worked so satisfactorily that we did not take further trouble to prepare partly digested albumen. Substituting this peptone solution for milk, we had a very delicate reagent and the resulting colored solutions were so clear as to be well adapted for comparisons in Nessler's tubes.

In the preliminary work, 1 cc. of the distillate or other solution to be tested was mixed with 5 cc. of a 1 per cent. peptone solution and 5 cc. of concentrated HCl containing one part FeCl<sub>3</sub> in 5000 parts acid. This mixture was gradually heated in a small flask over a free flame to from 80° to 85°, held at that temperature 2 minutes, and then allowed to cool. Thus we tested the following compounds closely related to formaldehyde or frequently accompanying it: acetic aldehyde, benzaldehyde, sucrose, dextrose, levulose, xylose, ether, ethyl and methyl alcohols, acetic, lactic, oxalic, propionic, glycolic, citric and benzoic acids, phenol, metol, pyrogallol, furfural, potassium cyanide and acrolein. Of these the glycolic acid and the ether are the only ones that gave the same color. The same sample of ether, after being thoroughly washed, ceased to give it. We conclude that the ether was contaminated with formaldehyde and probably the glycolic acid likewise. After the publication of the article by La Wall above referred to, in which he assigns furfural as the cause of Ramsey's supposed test for formaldehyde in caramelized sugar products; additional tests with furfural were made according to the details as finally worked out for this method and reported below. Though applied to solutions of furfural ranging in strength from 1 in 1,000,000 to 1 in 100, we got no reaction except the faint tint which water alone gives with the reagents. Assuming the ferruginized concentrated H<sub>2</sub>SO<sub>4</sub> reacts or fails to react in the same cases, we must conclude that La Wall was in error and that his furfural actually had formaldehyde in it, but not in sufficient quantity to show in the less sensitive test of Rimini, upon which La Wall depended to prove the presence or absence of formaldehyde. As ultimately applied to cane juice and sugar solutions, our method in detail is as follows:

The sugar solution is acidified with H<sub>3</sub>PO<sub>4</sub>, then distilled from a bath of boiling saturated common salt solution with a current of steam superheated to a temperature such that there will be but little change in the volume in the distillation flask. To 5 cc. of the distillate in a test tube, size 20 mm. by 180 mm., add 5 cc. of a 1 per cent. peptone solution (recently dissolved and filtered) and 10 cc. concentrated HCl containing 1 part FeCl<sub>3</sub> to 5000. Mix these with a

<sup>1</sup> C. r. d. l'Acad. des Science, **142**, 454-6. Chem. Centr., **1905**, I, 18, 131, 1178, 1423; **1906**, I, 917, 1193. Z. Ver. Rübenzucker Ind., **1906**, 93-103. Bul. de l'Assoc. des Chim. de Sucre. et de Dist., **23**, 649-652.

<sup>2</sup> Jr. Roy. Soc. N. S. W., (1907) **41**, 172-5. Intern. Sugar Jr., **11**, 100. Bul. de l'Assoc. d. Chim. de Sucre. et de Dist., **26**, 587.

<sup>3</sup> Am. J. Pharm., **81**, 384. Chem. Abstr., **3**, 2836.

<sup>4</sup> Chem. d. Zuckerarten, **2**, 1320.

<sup>5</sup> J. Soc. Chem. Ind., **26**, 3 and 4; Chem. Abstr., **1**, 750.

heavy glass stirring rod with rounded end, which may conveniently remain in the tube to weight it down and aid in mixing while heating in the water bath. Prepare likewise any number of other samples and at the same time a set of standards for comparison, which may conveniently include strengths 1 : 50000, 1 : 100000, 1 : 200000, 1 : 500000, 1 : 1000000, 1 : 2000000 and a blank. The test tubes, suspended through holes of an appropriate size in a board, are suspended in a water bath previously heated to such a temperature slightly above 82.5° C. that the cold tubes will bring it down to about 82.5°. Keep it in the bath at this temperature for altogether 5 minutes, occasionally shaking by a rotatory motion of the board so that the glass rods in the tubes will rotate and help mix the contents, then set into a bath of cold water. After cooling, the color intensities of each sample and its most nearly matching standard are matched in the ordinary way by varying the depths of the columns in Nessler's tubes. From these data the strength of the sample is determined. If the sample is stronger than 1 : 100000 it should be diluted tenfold or a hundredfold before mixing and heating, to bring it within the range 1 : 100000 and 1 : 1000000. As the dilute solutions of formaldehyde do not keep well, the tests should be made not too long after distilling and the standards should be made up from strong solutions not over a day or two prior to the time of using them.

An extended study of this method developed the following facts:

Blanks with the reagents available to us always gave a slight coloration, barely distinguishable from that with a standard 1 : 500000. Practically the method is not applicable to solutions weaker than 1 : 1000000.

With solutions of formaldehyde stronger than 1 : 100000 and reagents of same strength as before indicated, the increase in intensity of color is not correspondingly great. Instead of a deeper color, it develops a color less towards the violet and more towards the purple shade. Diluting afterwards to like strengths will not bring such pairs to like intensities of color.

Stronger solutions of formaldehyde with reagents stronger in both peptone and  $\text{FeCl}_3$  will develop a correspondingly greater intensity of color.

The proportion of  $\text{FeCl}_3$  to the peptone should not vary greatly from that given above to get best results.

Nitric acid may be substituted as the oxidizing agent for  $\text{FeCl}_3$ , using 1.6 cc. normal  $\text{HNO}_3$  to 100 cc. concentrated  $\text{HCl}$ , as was done by Shrewsbury and Knapp,<sup>1</sup> but, contrary to the conclusions of these gentlemen, we did not find the  $\text{HNO}_3$  possessing any

advantage, but having the disadvantage of decomposing and losing its activity quickly on standing after mixing with the  $\text{HCl}$ .

With the water bath as low as Shrewsbury and Knapp report, *viz.*, 50°, we found the action too feeble to be satisfactory, and likewise at 66°.

The color, after cooling, changes very slowly towards blue and less intensity, allowing one or two hours after heating to make the comparisons, provided, however, that sample and standard stood equally long.

Heating the mixture over the free flame in a casserole, controlling the temperature by the aid of a thermometer, gave less good results and was far less expeditious where many samples and standards had to be prepared.

In these experiments, in which superheated steam was used, the steam was superheated, for want of a better way, by passing it through a copper spiral over a small flame. Its temperature was controlled by use of a thermometer in the current of the steam about 5 inches above the neck of the distillation flask and about 10 inches from the liquid through which it bubbled. The temperature at the thermometer was held at about 115°, never going above 120°, except in Nos. 5, 7, 9 and 10, in which it was held at 120° to 125°. With the distillation flask in a boiling water bath and the inflowing steam at 115°, the volume increased about 9 cc. for every 50 cc. distilled. With the boiling saturated brine bath and the steam at 115°, the volume decreased about 7 cc. for every 50 cc. distilled. Though we adhered in most of these tests, for the sake of uniformity and comparative results, to the one temperature, 115°, our recommendation is to choose a lower temperature, or, if necessary, to omit superheating the steam, so that the volume in the distillation flask may remain constant.

*Application in Examination of Cane Juices, Sugar-House Products and Special Mixtures.*—The test for formaldehyde, of course, could not be made in the presence of the sugar and other constituents of the juice, therefore distillation was necessary to separate the formaldehyde from interfering substances. Experiments were tried with and without previously acidifying and by distillations from free flame, from oil bath, by steam from oil bath, by superheated steam from water bath, and by superheated steam from brine bath.

In the preliminary work, while we were following the method of heating over the free flame and comparing samples and standards that were prepared in succession, the results were not always regular or conclusive, but among the following conclusions, those not based upon the results of the final tests reported in the accompanying table are based upon regularities in the results of the preliminary tests, such as seemed to justify the conclusions.

In all the distillations the mouth of the condensers

<sup>1</sup> *Analyst*, 34, 12-14. (This report came to our attention after practically all our work on the method was completed.)



touched, or nearly touched, the narrow neck of the receiver flask, but no further provision was made to guard against the escape of formaldehyde into the air.

In tests in distilling in this manner, moderately strong formaldehyde solutions (1 per cent.), acidified with phosphoric acid, and determining the formaldehyde in the distillate by the KCN-AgNO<sub>3</sub> method, the recoveries were 84, 91, and 102 per cent., respectively, in three tests.

If water is distilled with superheated steam from a 10 or 15 per cent. sugar solution, not acidified, there are only traces of formaldehyde shown in the distillate (Nos. 5, 6 and 11 in the table).

In distilling an acidified juice or sugar solution from the direct flame (Nos. 1 and 4), the succeeding fractions of the distillate increase in the amount of formaldehyde as the caramelization point is approached. The browned residue, redissolved and again subjected to distillation, yields distillates relatively strongly charged with formaldehyde Nos. 1a, 2a and 3a). These results seem to bear out the conclusions reached by Trillat and Ramsey, cited above, with reference to the formation of formaldehyde in the caramelization of sugar. However, we are still not quite sure that this caramelization prod-

uct, the distillate from which gives the formaldehyde reaction, is actually formaldehyde, though we are satisfied it is not furfural. It does seem strange, if formaldehyde is formed by very slight caramelization in such large quantities as indicated by Nos. 1a and 2a in the table, that jams, caramel candies, and many other sweetmeats can be eaten with such impunity as they are.

In distilling sugar solutions with superheated steam, the distillates show only traces of formaldehyde and succeeding fractions are nearly constant in formaldehyde content (Nos. 7 and 12). In 250 cc. of distillate with superheated steam through a solution of 15 grams sugar in 100 cc. water, only 0.143 mg. formaldehyde was formed.

A number of other samples of fresh juice not recorded in the table, including one from green top joints of cane, gave results not remarkably different from No. 1 here reported.

In preliminary tests in which formaldehyde was added to water and to sugar solutions, there was evidence that sugar tended to hold back a small portion of the formaldehyde from distilling over.

Adding formaldehyde to cane juice or sugar solutions in the proportion of 1 mg. per 100 cc., it is recovered in the distillate either from direct distilla-

TABLE OF FORMALDEHYDE DETERMINATIONS.

			Formaldehyde found in fractions of distillate.						CH <sub>2</sub> O recovered, mg.
No. of test.	Composition of mixture.	Manner of distillation.	In 1st 50 cc. mg.	In 2nd 50 cc. mg.	In 3rd 50 cc. mg.	In 4th 50 cc. mg.	In 5th 50 cc. mg.		
1.	200 cc. juice + 5 cc. H <sub>3</sub> PO <sub>4</sub> <sup>2</sup> .....	Direct overflame	0.025	0.100	0.250	.....	.....	0.375	
1a.	Residue from 1 + 170 cc. water.....	" "	0.50	0.50	0.50	.....	.....	1.50	
2	200 cc. juice + 2 mg. CH <sub>2</sub> O + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	" "	0.86	0.94	0.96	0.30	0.16	3.22	
2a.	Residue from 2 + 170 cc. water.....	" "	0.50	0.50	0.50	in 15 cc.	in 6 cc.	1.50	
3.	200 cc. juice + 2 mg. CH <sub>2</sub> O.....	" "	0.39	0.81	0.66	0.19	0.08	2.13	
3a.	Residue from 3 + 170 cc. water.....	" "	0.62	0.63	0.57	in 15 cc.	in 6 cc.	1.82	
4.	20 g. sugar I <sup>3</sup> + 200 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	" "	0.059	0.190	0.270	.....	.....	0.519	
5.	10 g. sugar I + 100 cc. water.....	Superheated steam and in water bath	0.009	0.010	0.009	.....	.....	0.028	
6.	Duplicate of 5.....	Superheated steam and in water bath	0.012	0.011	0.011	.....	.....	0.034	
7.	10 g. sugar I + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in water bath	0.025	0.028	0.027	0.027	.....	0.107	
8.	Duplicate of 7.....	Superheated steam and in water bath	0.021	0.027	0.028	.....	.....	0.076	
9.	10 g. sugar I + 100 cc. water + 1 mg. CH <sub>2</sub> O.....	Superheated steam and in water bath	0.36	0.35	0.20	0.21	.....	1.12	
10.	10 g. sugar I + 100 cc. water + 1 mg. CH <sub>2</sub> O + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in water bath	0.53	0.37	0.21	0.18	.....	1.29	
11.	15 g. sugar II <sup>4</sup> + 100 cc. water.....	Superheated steam and in brine bath	0.008	0.008	0.008	.....	.....	0.024	
12.	15 g. sugar II + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.025	0.025	0.028	0.033	0.032	0.143	
13.	15 g. sugar II + 100 cc. water + 1 mg. CH <sub>2</sub> O + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.46	0.27	0.14	0.09	0.08	1.04	
14.	15 g. sugar run, after 5, made without CH <sub>2</sub> O + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.000 <sup>1</sup>	0.025 <sup>1</sup>	0.028	0.043	0.047	1.43	
15.	15 g. sugar, run 6, made with CH <sub>2</sub> O + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.007 <sup>1</sup>	0.030 <sup>1</sup>	0.047	0.054	0.054	0.192	
16.	15 g. molasses, run 5, made without CH <sub>2</sub> O + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.000 <sup>1</sup>	0.008 <sup>1</sup>	0.031	0.028	0.025	0.092	
17.	15 g. molasses, run 6, made with CH <sub>2</sub> O + 100 cc. water + 5 cc. H <sub>3</sub> PO <sub>4</sub> .....	Superheated steam and in brine bath	0.027 <sup>1</sup>	0.100 <sup>1</sup>	0.118	0.123	0.100	0.468	

<sup>1</sup> In these fractions of the distillate there was a slight cloudiness and probably interference with the test.

<sup>2</sup> The H<sub>3</sub>PO<sub>4</sub> solution in each case was an 85 per cent. sol.

<sup>3</sup> Sugar I is commercial refined sugar from the local market.

<sup>4</sup> Sugar II is commercial sugar from India.

tion or from distillation with steam, in such amounts that the tests, quantitatively applied, can serve easily to distinguish between products to which it has, and those to which it has not been added (Nos. 2, 10 and 13, and Nos. 1, 4, 7 and 12). From these acidified formaldehyde solutions, the formaldehyde comes off most copiously in the first fractions. When not acidified this is less marked and the total recovery is less in the same total volume of distillate (cf. Nos. 3 and 9). When made alkaline with NaOH, as we did in some preliminary trials, the tendency to hold back formaldehyde in the sugar solution was many fold greater.

Coming now to the main question which concerned us, *viz.*, Does formaldehyde added to juice in the sugar-house all boil away or does it persist in any final salable products? we seek the answer in tests Nos. 14 to 17.

Runs 5 and 6 were made at the small mill of the Louisiana Sugar Experiment Station, the former without the addition of any formaldehyde either in that or the immediately preceding run, and the latter with the addition of formaldehyde to the fresh juice in the proportion of about 1 part of formalin (40 per cent. sol. of formaldehyde) to 160,000 parts of juice, or 25 parts  $\text{CH}_2\text{O}$  to a million. The clarification in each run was as usual with sulphurous acid, followed by liming back almost to neutrality. The concentration was accomplished as usual with reduced pressure in the "effects" and vacuum pan. The sugars used in these experiments (Nos. 14 and 15) are the first sugars, testing about 96 per cent., and the molasses samples (Nos. 16 and 17) are of the first molasses in each case, testing about 43 per cent. sucrose and 58 purity. In the distillation with superheated steam and the formaldehyde determination in these samples, carried out as above described, a peculiar condition developed which was not noted in the previous samples with pure sugar solutions. The first one, or two fractions of the distillate, were slightly cloudy, and these same fractions, which should have been highest in formaldehyde, gave no reaction, or only very weak ones for that substance. This leads us to suspect that our test in these cases does not show the total quantities of formaldehyde present. Suspecting that the interfering substance may be sulphurous acid, or possibly other sulphur compounds, tests were made and it was found that the addition of sodium sulphite strongly interfered, that sodium thiosulphate completely prevented the color development, and that hydrogen sulphide but slightly affected the intensity of the reaction. Notwithstanding these probable shortages in the total formaldehyde recovered, we still find evidence of an excess of formaldehyde in the products from juice to which it had been added, very small in the case of the 1st sugar, but more pronounced in the case of

the 1st molasses. In the 1st sugar it amounts to 12.8 parts  $\text{CH}_2\text{O}$  per million as against 9.5 parts per million in 1st sugar from juice without added formaldehyde, or an excess of 3.3 parts per million. In the first molasses it amounts to 31.2 parts per million as against 6.1 parts per million in 1st molasses from juice without added formaldehyde, or an excess of 25.1 parts per million. The molasses is thus found to be as strongly charged with this excess of formaldehyde as was the juice from which it was made. Assuming that the yields of 1st sugar and 1st molasses are 9.5 per cent. and 6 per cent., respectively, of the juice, then the amounts of formaldehyde retained by them are about 1.2 per cent. and 6 per cent., respectively, of that added to the juice, or a total of 7.2 per cent., which, as far as these tests show, was not boiled away. It is probable, as pointed out above, that these tests show only part of that actually retained. The small quantity left in this 96 per cent. sugar may justify the conclusion that in refining the sugar this excess is all eliminated.

If the sugar is the only product used for food, then there need be no hesitation, on the score of health considerations, in using formaldehyde as a preservative in juice in the sugar mill. If, however, the molasses is also to be used for food, or if table syrup is to be manufactured, then the question of the permissibility of its use may reasonably be raised. To this question we deem the data now at hand to be insufficient basis for a definite answer. We should have the results from further tests of final and of intermediate products. We should develop a method to circumvent the interference of sulphurous acid or other substances in the distillates, in the formaldehyde determination. We should make comparative tests also with syrup or molasses and sugar made by the open kettle method of boiling, with and without formaldehyde. We should, moreover, know in what form or combination the formaldehyde is held back in these sugar solutions, and whether it is deleterious to health in this form or combination.

#### SOME EFFECTS OF FEEDS UPON THE PROPERTIES OF LARD.

By C. L. HARE.

Received April 11, 1910.

It is well known that in the feeding of hogs different feeds produce varying effects upon the carcasses of the animals and upon the characteristics of the fats produced.

The Department of Animal Industry of the Alabama Polytechnic Institute has through a series of years made extended experiments in pork production, particularly from an economic standpoint.

Working in cooperation with that department, there have been encountered lards which show interesting effects of the feeds used in their production.

The following is a preliminary account of the investigation undertaken to point out some changes in properties so brought about.

Among the available pork producing feeds some of the most important economically are corn, peanuts, soy beans, cottonseed-meal and tankage, the three last being relatively rare as constituents of rations for hogs.

The results here given were secured on lards resulting from three series of feeding experiments in each of which series these feeds were used.

In the first series of experiments examination was made of lards from thirty-six hogs.

The pigs in this series were divided into six lots and the feeding so conducted as to show the effect upon the lards of corn, cottonseed-meal, tankage, soy beans and peanuts. The lots were further subdivided so as to show the effect of corn following peanuts, of cottonseed-meal following peanuts, and of tankage following soy beans and peanuts.

In the second feeding trials results were again obtained on thirty-six pigs—the feeding in this series being intended to show the effects of, 1st corn, 2nd cottonseed-meal, 3rd tankage, 4th soy beans with varying rations of corn, 5th soy beans and peanuts, 6th soy beans and peanuts with a finishing ration of corn, 7th soy beans and peanuts with a finishing ration of corn and cottonseed-meal, 8th soy beans and peanuts with a finishing ration of corn and tankage.

The third experiment included twenty-three pigs and data were secured illustrating the effects of, 1st, corn; 2nd, tankage, 3rd, cottonseed-meal; 4th, soy beans with varying amounts of corn; 5th, soy beans with a finishing ration of corn; 6th, soy beans with a finishing ration of corn and cottonseed-meal; and 7th, soy beans with a finishing ration of corn and tankage.

Corn being the universal hog feed, one corn-fed lot was carried in each series as a basis of comparison—the corn lards being used as standards.

In every series of experiments the feeding of each lot was so conducted and the slaughtering so regulated in point of time that the full effect of the ration might be observed. Thus, in the corn-fed lot of series No. 1 the pigs were slaughtered at intervals—the first at the end of thirty-five days and the last at the end of one hundred and forty-seven days.

Slaughtering one pig from each lot at stated intervals furnished lards on which comparable results could be secured from all pigs in the different lots as well as in the same lot.

The period of feeding in days for each pig is indicated in the tables.

The rations of corn, cottonseed-meal and tankage were fed soaked.

The pigs were made to graze the soy beans and peanuts.

All pigs in each series entered the feeding trials at a fairly uniform age and weight.

All lards were rendered from the kidney fat and thus represent uniformly the firmest fat obtainable from the pig.

Since the melting points and iodine values of lards are more notably affected by feeds than are the other characteristics, and at the same time probably furnish a more accurate index to the qualities of lards than do the other constants, these values were selected as giving a sufficient showing of the changes produced.

In Table I are found results on lards from hogs which had been fed on corn for periods varying from 35 to 150 days. The results include lards from three feeding trials.

The lards in series 2, with the exception of those numbered 61, 42, 53, 15, 23, and 34, had become slightly rancid when the iodine values were determined, but it is not thought that the oxidation had proceeded so far as to seriously affect those values.

No days fed.	No. of pig.	Melting point	Iodine value.	Series.	Ration.
63	101	43.5	53.87	1	Cornmeal
91	103	43.4	58.68		
119	106	44.2	57.60		
140	105	41.6	57.37		
147	104	40.5	57.10		
Av.,			56.92		
35	72	43.1	56.50	2	Cornmeal
70	71	44.8	51.50		
84	73	44.0	49.70		
112	75	43.0	56.00		
134	74	....	56.57		
Av.,			54.05		
75	69	....	64.79	3	Cornmeal
110	36	....	63.07		
125	42	....	60.04		
150	8	....	60.07		
Av.,			61.98		
Average,			57.35		

Examination of these figures seems to show that corn as fed in these trials has not the effect of softening pork to the extent indicated by results secured by some investigators, notably those of Shutt<sup>1</sup>

On the other hand, the iodine values are somewhat below the average value of that constant for lards—this being particularly true of the lards in series 2, which gave an average iodine value of only 54.05. Not only do the melting points and iodine values indicate relatively firm lards throughout but the pigs which were fed corn continuously for a period of five months show no greater degree of softness than those fed for shorter periods on this ration.

In fact, the pigs in series 3 show an increasing firmness in the fat, though this may be attributed to the increasing age of the animal.

Table II shows the effect upon the two constants under consideration of a ration containing much cottonseed-meal.

<sup>1</sup> Canada Cent. Ex. Sta., Bull. 38.



TABLE II.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	112	47.7	61.00	1	Cornmeal 2/3, cottonseed-meal 1/3.
63	109	49.8	53.57		
91	111	49.3	53.57		
119	110	48.3	57.58		
140	108	50.0	55.16		
147	107	46.8	55.95	2	
35	61	49.2	48.44		
70	65	50.8	51.20		
84	64	50.0	51.60		
112	62	49.6	50.22		

Average, 53.80

This mixture contains a very little more oil than the corn ration but constitutes a much higher protein ration. It will be observed that the melting points are materially elevated, while the iodine values suffer a corresponding depression.

This tendency has been often observed in this as well as in other rations where the protein content has been increased—*e. g.*, corn and skim-milk, and is even more apparent in a ration containing much smaller amounts of cottonseed meal than the above.

Table III gives results on lards produced by a ration consisting of corn 9/10 and cottonseed-meal 1/10.

TABLE III.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
70	45	48.6	53.80	2	Cornmeal 9/10, cottonseed-meal 1/10.
84	41	48.4	50.60		
112	44	47.6	55.0		
134	40	49.0	52.0	3	
99	42	49.7	41.85		
75	39	....	49.23		

Average, 52.13

Here we find the results on iodine values lower than where a more concentrated cottonseed-meal ration was fed. It is, however, probable that with results on a larger number of lards from this ration more comparable figures would be secured, as there is no apparent explanation of this slight difference in properties.

In order to test further the effects of a feed containing more protein than corn, one lot of pigs in each series was fed a mixture consisting of corn 9/10 and tankage 1/10. Table IV gives analytical results on the lards produced.

TABLE IV.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	131	43.1	59.08	1	Cornmeal 9/10 Tankage 1/10
63	132	45.6	50.06		
91	136	42.5	56.59		
119	135	41.6	57.80		
140	133	45.1	57.77		
35	53	....	49.85	2	
70	54	43.0	56.80		
84	51	42.9	56.53		
112	52	....	56.53		
91	50	42.2	52.40		
91	55	41.4	58.80	3	Same
75	1	....	57.02		
110	43	....	61.25		
125	37	....	52.26		
150	2	....	53.61		

Average, 55.67

The figures in this table again seem to indicate that the introduction of a high protein feed into the ration produces an elevation of the melting point and depression of the iodine value of lards. While the effect upon these two constants is not so pronounced as in the case of cottonseed-meal they are nevertheless significant and would seem to point to the presumption that the changes in properties brought about in fats by cottonseed meal are, at least in part, due to the protein content of that feed.

For purposes of comparison, the averages on all lards produced from the four rations so far discussed are presented in Table V:

TABLE V.

Ration.	Iodine value.	Average of
Cornmeal.....	57.35	14 lards
Cornmeal 2/3 Cottonseed-meal 1/3	53.83	10 lards
Cornmeal 9/10 Cottonseed-meal 1/10	52.13	5 lards
Cornmeal 9/10 Tankage 1/10	55.67	15 lards

The increasing use of soy beans as a hog feed makes necessary the determination of the effect of this ration upon the finished product and a study of rations which may be suited to finishing hogs which have been fattened thereon.

Table VI gives figures obtained on lards from pigs grazed on soy beans and at the same time fed part rations of cornmeal:

TABLE VI.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	34	33.67	100.5	2	Soy beans and 1/4 ration of corn
75	76	?	94.86	3	
35	125	41.8	71.09	1	Soy beans and 1/2 ration of corn
35	23	40.0	80.60	2	
75	87	?	82.70	3	Soy beans and 3/4 ration of corn
35	15	40.7	79.0	2	
75	68	?	84.32	3	

Average, 84.72

Representing as these values do results on lards the firmest obtainable from the pigs—that rendered from the kidney fat—they illustrate the very great softening effect of this feed upon the fat.

Some of the lards in this lot remain semi-fluid throughout the winter months and are too soft for melting point determinations.

Whether the softness is due solely to the oil in the feed or in part to the fact that it is grazed as a green feed has not yet been determined. It is probable, however, that both factors influence the properties of the lard. This would be in keeping with Shutt's results on pigs grazed on clover. Further, his observations that certain other green crops, as turnips and sugar beets, have no softening effect upon lards are confirmed by data secured in this laboratory from pigs grazed on sorghum.

This leads to the suggestion of the possibility that

the legumes when fed green to hogs have a softening effect upon the fat.

While the soy bean feed is high in oil content, it is also relatively high in protein. The results therefore in a measure contradict the assumption that protein in the feed induces hardness in the fat. This further suggests the question whether the protein molecule in this feed breaks down into cleavage products differing from those formed by cleavage of the protein molecule of corn and tankage and, in turn, produces radically different effects upon the fat.

In order to determine the persistence of the softness of fat produced by soy beans, three different finishing rations were employed: corn, cottonseed-meal and tankage.

Table VII illustrates the effect of corn in hardening the fat:

TABLE VII.

Ration—Soy bean grazing and 1/4 ration of corn followed by corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	76	94.86	3	Corn 35 days
75	98	83.92		Corn 50 days
75	88	69.77		Corn 75 days
75	.	70.31		
Average of corn fed lot in this series		61.98		

The limited number of pigs in this lot renders the results none the less valuable, inasmuch as they are fully confirmed by the figures in Table XI, which show the effect of corn following soy beans and peanuts.

Although these results show that corn produces a marked hardening effect, yet a comparison of the iodine values on numbers 88 and 7 with the average value of the corn-fed lot of this series, indicates that the properties conferred by the soy bean ration have in some measure persisted even after a period of 75 days' feeding on corn.

Some difficulty was experienced in testing the hardening effect of cottonseed-meal as in this series nearly all pigs on a ration of this feed died of cottonseed-meal poisoning.

However, two cottonseed-meal pigs in this trial made good growth and Table VIII sets forth the results secured on these:

TABLE VIII.

Preliminary ration soy bean grazing and 1/2 ration of corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	87	82.70	3	Cornmeal 2/3
75	88	73.41		Cottonseed-meal 1/3 for 35 days
				Cornmeal 2/3
75	56	65.46		Cottonseed-meal 1/3 for 50 days
Average of corn lards of this series.		61.98		

The effect of the cottonseed-meal ration is what

was expected and the hardening effect would possibly have been greater could the time of feeding cottonseed-meal have been extended.

The softness induced by the soy bean ration is somewhat in evidence after 50 days' feeding on cottonseed-meal.

The effect of tankage, the third finishing ration used in these experiments, is set out in Table IX:

TABLE IX.

Preliminary ration—Soy bean grazing and a 3/4 ration of corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	68	84.32	3	Cornmeal 2/3
75	87	68.83		Tankage 1/3 for 35 days
75	66	72.67		Cornmeal 2/3
				Tankage 1/3 for 50 days
75	77	74.0		Same 75 days
Average values of corn lards.		61.98		

Here again there is illustrated the pronounced hardening effect of a high protein ration.

For some unexplained cause the hardening effect in this trial with tankage seems to be greatest at the end of 35 days' feeding period and the lards to increase in softness for longer periods of feeding. This is probably due to individual peculiarities of the pigs. There still appears a persistence of the properties originally contributed by soy beans.

A study was also made of the persistence of the properties conferred upon lards by a ration of soy beans followed by peanut grazing.

There is first given in Table X values obtained from pigs slaughtered off peanuts following soy beans:

TABLE X.

Ration—Soy bean grazing followed by peanut grazing.

No. of days fed soy beans.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
35	127	40.6	79.61	1	Peanuts 28 days
35	25	31.27	89.84	2	Peanuts and 1/2 ration corn 35 days
35	14	37.0	76.94	2	Same
35	33	?	89.70	2	Same
Average.			84.02		

A comparison of these lards with those from the soy bean fed pigs, as shown in Table VI, demonstrates that while the average results of the two sets are practically the same, yet some of the individual soy bean lards are very materially softer than the softest of this lot, and that as between soy beans and peanuts the former has probably the greater softening effect.

In efforts to harden the fat of the pigs fed upon both soy beans and peanuts, use was again made of corn, cottonseed-meal and tankage.

The effect of corn is shown in Table XI:

TABLE XI.

Ration—Soy beans followed by peanuts followed by corn.

No. days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	14	37.0	76.94	2	
70	10	36.9	82.80	2	Corn 14 days
70	12	36.8	73.93	2	Corn 42 days
70	11	39.0	70.1	2	Corn 64 days

There is found here a confirmation of the results recorded in Table VII, which illustrate the hardening effect of corn as well as the difficulty of hardening the fats to a normal firmness—using the corn lards as standard.

The effect of the corn is progressive and is greatest as in Table VII during the first forty to fifty days.

Still further confirmatory results on the effect of corn were secured from a third trial with four pigs. The results are recorded in Table XII:

TABLE XII.

Ration—Sorghum and 1/2 corn 35 days. Peanuts and 1/2 corn 28 days (preliminary).

No. days fed preliminary ration.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
63	113	40.8	70.08	1	
63	116	41.8	62.15	1	Corn 28 days
63	117	42.3	60.67	1	Corn 56 days
63	118	42.7	60.60	1	Corn 77 days

In Table XIII are given results secured on the soy bean peanut pigs, finished on a ration of  $\frac{2}{3}$  corn and  $\frac{1}{3}$  cottonseed-meal.

TABLE XIII.

Days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	25	31.2	89.84	1	
70	22	42.4	76.1	2	2/3 corn and 1/3 Cottonseed-meal for 42 days
70	21	41.5	79.22	2	Same for 64 days

These results are not so striking as those found in Table VIII, but the one set is confirmatory of the other. Cottonseed-meal in the ration exercises its usual function of firming the fat.

The lot in this series finished on tankage puts this feed in a most favorable light as a finishing ration, as will be observed by inspection of the figures in the following table:

TABLE XIV.

Preliminary ration—Soy beans 35 days followed by peanuts 35 days.

No. days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	33	....	89.70	2	
70	35	39	74.35	2	Corn and 1/3 tankage 42 days
70	31	41.0	70.65	2	Same 49 days
63	127	40.6	79.61	1	Corn and 1/6 tankage 28 days
63	126	41.9	66.40	1	Same 77 days
63	130	42.9	64.69	1	

While, as before stated, these results point to tankage as a desirable ration for hardening the fat of soft hogs yet, on considering them in connection

with the results in Table IX, it is seen that confirmatory feeding trials are necessary before the results in Table XIV can be accepted.

Tankage, however, is free from the toxic effect which renders cottonseed-meal a dangerous hog feed and the data secured are sufficient to emphasize its value as a finishing ration. The results too show that it compares favorably with cottonseed-meal in its hardening effect on the fats. This, however, is not verified by examination of the carcasses nor by the results on pigs fed these rations without a prior softening ration—see Table V—and further comparative feeding trials are in progress.

Below is given a further comparison of lards from the two feeds:

TABLE XV.

Preliminary ration—Soy beans 35 days. Peanuts 35 days. Corn 14 days Days fed soy beans.

peanuts and corn.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
84	32	36.9	82.80	2	
84	10	39.2	71.60	2	Corn 2/3, tankage 1/3 for 14 days.
84	20	44.4	71.80	2	Corn 2/3, Cottonseed-meal 1/3 for 14 days.

The results on this lot of three pigs but serve to further confirm results recorded in the foregoing tables illustrative of favorable changes produced in the properties of lards by these two rations.

Summarizing the results, it is found that corn may be fed without regard to time limit in so far as concerns any unfavorable effect on the properties of the lard.

Soy beans and peanuts both produce oiliness in the hogs and the lards resulting are extremely soft.

The fat of oily hogs can be hardened by rations of corn, cottonseed-meal or tankage—the two latter producing unusually firm lards.

The possibility is suggested that legumes when fed green may produce soft fats.

In connection with the general subject here discussed, there are presented below results which accentuate the extreme differences in properties which may be conferred upon lards by different feeds:

No. of pig.	Melting point.	Iodine value.	Iodine value of liquid fatty acids.	Saponification value.
34	?	100.5	119	197.5
100	48.2	40.35	78	203.2

Pig No. 34 is selected from the soy bean fed lot.

No. 100 was fed throughout its life on slaughter pen refuse and weighed about 200 pounds when slaughtered.

This lard presents much the appearance of beef tallow and its constants possess much the same value as those of beef fat. It further responds readily to the Belfield test for beef fat.



[CONTRIBUTION FROM THE LABORATORY OF SOIL CHEMISTRY, UNIVERSITY OF TENNESSEE, AGRICULTURAL EXPERIMENT STATION.]

## SOIL HUMUS AS DETERMINED BY DIFFERENT METHODS.

By SHERMAN LEAVITT.

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From the wide variation in analytical results on samples of several different types of soil when analyzed for percentage of humus by five well-known methods, the writer has been led to believe that these variations may be partly accounted for by the fact that the several methods may individually include or exclude certain organic substances as humus.

The Official method for humus,<sup>1</sup> based on that of Grandean, is, to my knowledge, followed by most of the soil chemists in this country at least to the completion of the extraction of organic matter with four per cent. ammonia. This method determines the organic matter by evaporation of a clear aliquot free from clay (a difficult result to obtain) and by burning off the organic matter in a platinum dish. We may therefore assume that soil humus is empirically the total organic matter, combined with a little inorganic matter, soluble in a solution of four per cent. ammonia at ordinary temperature. Thus far, I believe, all methods agree, however they disagree from this point.

As is well known, the Official method, when followed literally, is very unsatisfactory and gives abnormally high results. This is due to the presence of clay which cannot readily be removed by the method as given. Different investigators have accordingly modified this method more or less to overcome this difficulty. Among the modified methods may be mentioned those of Cameron and Breazeale;<sup>2</sup> Peter and Averitt;<sup>3</sup> Mooers and Hampton;<sup>4</sup> and C. W. Stoddart.<sup>5</sup> Briefly, the principal modification of each of these four methods is as follows:

Cameron and Breazeale filtered off the clay by means of a Pasteur-Chamberland filter and determined the humus in the filtrate free from clay.

Peter and Averitt used the Official method in connection with a correction factor of ten per cent. of the residue which is left after burning off organic matter and which must be subtracted from the total loss in weight. This factor seems to apply fairly well in some cases but, as Mooers and Hampton have shown, it does not apply to all soils.

Mooers and Hampton devised the method which is in use in this station. Briefly, the clay is partially removed by settling for several days, the supernatant liquid being then siphoned off. An aliquot portion of this liquid is then evaporated to dryness and baked for some hours on the steam bath. It is re-dissolved

in four per cent. ammonia, filtered, re-evaporated, baked again, dissolved in four per cent. ammonia, and filtered.

The solution should then be absolutely clear. When this method is properly handled, the insoluble residue remaining after burning off the organic matter in a platinum dish is not much over 0.20 per cent. of the total weight of soil taken.

C. W. Stoddart's method, as given in the article referred to, depends upon the use of a strong solution of ammonium sulphate to flocculate and precipitate the clay on standing twelve hours. The humus, as humic acid, is then precipitated out by the addition of strong hydrochloric acid to a clear aliquot of the solution free from clay and by whirling in the centrifuge, the resulting precipitate being filtered, washed, dried at 105° C., and weighed on a tared gooch crucible. This method would seem to be the ideal one for simplicity and the writer has striven to make this applicable to the soils of Tennessee, but without success.

Several of these methods have been respectively tried on the same soils by two chemists in this laboratory, working over a year apart, the results of each method being comparable. I shall take the liberty of quoting the results on two very different types of soils taken from the paper of Messrs. Mooers and Hampton and of placing them alongside the results obtained by the writer to better illustrate the point.

In the soils which they examined, Mooers and Hampton found the Official method unreliable; the method of Peter and Averitt only partially reliable; and the method of Cameron and Breazeale practically of no value. The writer finds that excellent results can be obtained with the Mooers and Hampton method after a little practice and has little trouble duplicating results on the same samples of soils which they used.

As stated before, the writer hoped to make use of Stoddart's method, which commends itself on account of its simplicity and ease of manipulation, but, as can be easily seen from the last column in the above table, the results obtained by Stoddart's method are not comparable to those obtained by the modified official method. This fact was also shown in the following way: Duplicate aliquots of ammonium humate solution from soil No. 602, freed from clay according to the method in use in this laboratory (Mooers and Hampton), were evaporated to dryness in platinum dishes, being heated in the oven for three hours and weighed. The weight of extract in each case was the same. One aliquot was burned and the organic matter as humus determined by loss on ignition, giving 1.22 per cent. humus. The other aliquot was completely dissolved in 50 cc. of four per cent. ammonia, the humus precipitated by hydrochloric acid, giving only 0.45 per cent. of humus as humic acid.

<sup>1</sup> Bull. 107 (revised edition) Bureau of Chemistry.

<sup>2</sup> J. Am. Chem. Soc., 26, 29-45.

<sup>3</sup> Kentucky Station, Bull. No. 126, p. 63-126.

<sup>4</sup> J. Am. Chem. Soc., 30, No. 5.

<sup>5</sup> J. Ind. Eng. Chem., 1, 72.

A qualitative test was made of this filtrate after removal of the excess of acid by evaporation and baking on the steam bath, and it was found to yield in a faintly acid solution a considerable quantity of greenish copper salt, which was organic. This showed qualitatively that all of the organic matter was not precipitated by the hydrochloric acid. That this wide variation between the weights of humic acid

In the above table is a column (No. 5) marked "percentage of humus compounds precipitated by copper after hydrochloric acid treatment" (the excess of acid having been removed by evaporating to dryness and baking on the steam bath). Several years ago it was shown by S. Suzuki<sup>1</sup> to be possible to obtain copper salts from humic acid derived from natural sources. Two of these salts were identified,

TABLE I.

Sample.	Character of soil	By the writer.									
		Official.		Factor 10, per cent.		Factor 14, per cent.		Filtration.		Moores and Hampton.	
		Humus.	Ash.	Humus.	Ash.	Humus.	Ash.	Humus.	Ash.	Humus.	Ash.
636	Fertile clay loam.....	2.04	5.23	1.52	1.31	0.64	0.22	1.36	0.28	1.61	0.96
	" " " ".....	2.34	6.75	1.66	1.40	0.65	0.18	1.33	0.19	2.15	0.75
	" " " ".....	2.64	7.97	1.84	1.51	0.77	0.21	1.38	0.23	.....	.....
	" " " ".....	2.55	8.78	1.67	1.32	0.59	0.24	1.26	0.33	.....	.....
602	Poor clay loam.....	1.28	1.95	1.08	1.01	0.76	0.23	1.08	0.29	1.65	3.99
	" " " ".....	1.26	2.06	1.05	0.97	.....	.....	1.11	0.18	1.67	3.93
	" " " ".....	.....	.....	.....	.....	.....	.....	.....	.....	1.41 <sup>2</sup>	6.45
	" " " ".....	.....	.....	.....	.....	.....	.....	.....	.....	0.97	.....
	" " " ".....	.....	.....	.....	.....	.....	.....	.....	.....	0.94	.....

and the ammonium humate could not be accounted for by the presence of the ammonium radicle, was shown by dissolving the humic acid on the gooch crucible in four per cent. ammonia, evaporating, drying and weighing as ammonium humate, very little increase of weight being noted.

The writer has attacked this problem in a slightly different manner. Four large samples of ammonium humate, prepared from distinctly different important types of soils, were used. The samples were made from 500 grams of air dried soils by the Official method and were freed from clay by repeated treatments of baking on the steam bath to flocculate the clay and to bring about its removal by filtration, this operation requiring about six weeks on account of the large amounts of soils taken. These residues were finally dissolved in water and made up to 500 cc. each and allowed to stand about two months tightly stoppered to further clarify the solution.

The clear solutions were pipetted off for analysis and the amount of humus as ammonium humate and of ash present were determined in each cubic centimeter by evaporation and loss on ignition. Known amounts of each soil humus were diluted to 50 cc. and treated with 2 cc. of concentrated hydrochloric acid, whirled in the centrifuge, filtered, washed with 1 per cent. hydrochloric acid, and dried according to Stoddard's method. The following tabulated results were obtained:

one being a salt of active prolin, and the other probably a salt of inactive prolin. There was also formed a considerable quantity of copper salts of unknown acids. The same investigation brought out the fact "that the nitrogen in the humus is not as amino compounds but chiefly as a kind of protein which may be connected more or less intimately with the black substances."

The writer of the present article has been led to believe from the type soils that have come under this investigation that many of them contain their humus largely in the form of protein or like proteins. This would account, in part, for some of the very low determinations of humus by Stoddard's method. As some of the proteins can be precipitated as copper salts, the results given in column 5 probably represent the total organic matter as protein or like proteins (the actual weight of copper in combination having been determined in each case and subtracted), including some organic acids precipitated as copper salts which have failed of precipitation by hydrochloric acid. Column 8 gives the percentage of organic matter by difference, not precipitated by hydrochloric acid and copper collectively. Column 7 gives the percentage of total humus and protein bodies which can be salted out from the humus solutions by means of an excess of ammonium sulphate. This method is given as a quantitative one<sup>3</sup> for removing all protein bodies except peptones from solution.

TABLE II.

Locality.	Sample.	Per cent. humus in soil.	Wgt. of humus used.	Ash in humus used.	Per cent of total by HCl.	Per cent. humus compounds by copper.	Per cent by HCl + Cu.	Humus by salting with (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	Organic matter not precipitated.
Cookeville.....	1096	0.93	0.0369	0.0066	45.81	34.83	80.64	70.4	19.36
Crossville.....	1101	0.90	0.0238	0.0012	26.05	25.22	51.27	33.6	48.73
Jackson.....	1266	0.39	0.0280	0.0025	64.28	19.29	83.57	75.0	16.43
Gallatin.....	1267	1.66	0.0392	0.0021	49.74	50.00	99.74	57.9	0.26

<sup>1</sup> Bulletin College of Agriculture, Tokyo Imperial University, 7, (No. 4) 513-529.

<sup>2</sup> This result was abnormally high due to a little clay left in solution before the writer had become thoroughly familiar with the method.

<sup>3</sup> Watts' Dictionary, "Proteids."

As Stoddart's method calls for the use of considerable ammonium sulphate to flocculate and precipitate, the clay, we have another explanation of the low results obtained when this method is used on soils of this type, *i. e.*, where the humus is probably largely of a protein nature.

The above table shows very clearly that the humus matter in each of the soils given is quite different. This can be shown distinctly to the eye in the case of soils 1101 and 1266. If we use the same weight of humus from each soil and dilute them to the same volume, say 50 cc.; the solution made from the humus from soil 1266 will be black and cannot be seen through in a 250 cc. beaker, while the same weight of humus from soil 1101 will be a light amber, perfectly transparent (see column 4 of table for corresponding percentages precipitated by hydrochloric acid).

We notice in column 8 of this table for soil 1101 that about 49 per cent. of the organic matter is unaccounted for, whereas in soil 1267 apparently nearly all of the organic matter has been precipitated by hydrochloric acid and as a copper salt. The writer is inclined to believe that the humus from soil 1101 is in a higher state of oxidation than that from the other soils and that it is partly present as highly oxidized organic acids. This study is being continued in this laboratory.

The writer wishes to express his thanks to Professor Charles A. Mooers, of this station, for introducing the writer to the chemistry of soil humus and for kindly reading and criticizing this paper.

Mr. H. H. Hampton, now at the Johns Hopkins University, Baltimore, Md., gave the writer many helpful suggestions regarding the technique of the Mooers and Hampton method for humus.

Professor William R. Orndorff, of Cornell University, has very kindly gone over many points on this subject with the writer.

KNOXVILLE, TENNESSEE  
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## ON THE COMPOSITION OF LIME-SULFUR SPRAY.

By H. V. TARTAR AND C. E. BRADLEY.

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**Introduction.**—The literature on the composition, properties, and use of the commercial lime-sulfur spray solution, now so widely employed as an insecticide and fungicide, consists in the main of the details of field experiments which have been carried out in various localities by entomologists and horticulturists. In the majority of these tests but little attention has been given to the composition of the spray. The solution has been made by boiling, either by direct heat or with live steam, sulfur and freshly slaked lime in water. These materials have been used in varying proportions. In some instances

the quantity of lime and of sulfur used, together with the specific gravity of the resulting solution, have been stated. Other than this, it has been the prevailing practice to give but little attention to the composition of the spray, and up to the present time there have been no definite systematic field experiments to show the relative insecticidal and fungicidal value of its constituents. The real chemical investigations dealing directly with the lime-sulfur solution have been carried out by Avery, Haywood, Thatcher, Giboney, and Wellington.

Avery<sup>1</sup> modified standard methods of analysis to suit the conditions so that the total sulphur and total lime could be determined.

Haywood<sup>2</sup> was the first investigator to point out the real constituents of the spray solution now in use. He showed that it contained considerable amounts of polysulfids and thiosulfate, and but small quantities of sulfate and sulfite of calcium. A small amount of calcium hydroxide was supposed to be present. It may be stated here that the compounds which are formed when sulfur and calcium hydroxide are boiled in aqueous solution had been quite thoroughly investigated by Divers<sup>3</sup> and others previous to Haywood's work on the commercial spray solution. Standard methods of analysis were modified by Haywood so that quantitative estimations could be made of the sulfur combined as sulfids and polysulfids, as thiosulfate, as sulfate and as sulfite, respectively. The presence of sodium chloride was found not to affect the composition nor the amount of the sulfur compounds in the solution. Different formulas for the preparation of the spray were tried and the use of 1 part of lime to 1 1/4 parts of sulfur was suggested for practical purposes. Solutions made from commercial materials were found to be of the same composition as those made from chemically pure materials. One hour of cooking was demonstrated to be sufficient time to effect the combination of the sulfur with the lime.

Perhaps the most valuable part of Haywood's work was his study of the decomposition of the spray by the use of artificial experiments approximating the conditions on the tree. He found that the principal immediate products of decomposition were calcium thiosulfate and free sulfur, and that the thiosulfate gradually decomposed to form sulfite and liberate more sulfur. The calcium sulfite finally oxidized to the sulfate. From the results obtained, a theoretical explanation of the action of the wash on insects was made. Haywood also suggested the preparation of a spray in which sodium hydroxide was substituted for slaked lime.

Thatcher<sup>4</sup> showed previous to Haywood that sodium

<sup>1</sup> Bull. 90, Bureau of Chemistry.

<sup>2</sup> J. Am. Chem. Soc., 1905, page 244. Bull. 101, Bureau of Chemistry.

<sup>3</sup> J. Chem. Soc., 1884, page 270.

<sup>4</sup> Bull. 56, Washington Station.



chloride did not affect the quantity of sulfur compounds in solution. Later<sup>1</sup> Thatcher demonstrated that 1 part of lime to 1.95 parts of sulfur was the proper proportion of chemically pure materials to be used. The present extended commercial use of 1 part of lime to 2 parts of sulfur in the preparation of the spray attests the correctness of Thatcher's conclusion. In 1908<sup>2</sup> he endeavored to work out the exact reaction between lime and sulfur when boiled in aqueous solution. It was found that perhaps the following primary reaction takes place:



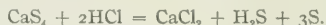
The analysis of concentrated lime-sulfur spray solutions<sup>3</sup> revealed the fact that a secondary reaction occurs in which the amount of thiosulfate decreases while the polysulfids increase. Thatcher made some suggestions regarding the nature of this reaction but, because of the lack of sufficient analytical methods, was unable to present any definite results.

Giboney,<sup>3</sup> from the results of laboratory experiments, suggested that 40 minutes is the proper length of time for boiling the solution. He also gave analytical methods for estimating the "sulfid" and "polysulfid" sulfur in the polysulfids. Prolonged boiling was found to effect the solution of a little more calcium and thus cause the formation of somewhat lower sulfids. Giboney also demonstrated the harmful effects of magnesia on the composition of the solution and pointed out the necessity of using lime which is comparatively free from this substance.

Wellington<sup>4</sup> stated that lime-sulfur-salt wash contains 25 per cent. to 30 per cent. of calcium monosulfid and hydrosulfid collectively. This view has not been upheld by any other investigator and is, no doubt, erroneous. Wellington assisted by Fernald showed, however, by field experiments, that calcium thiosulfate does possess some insecticidal value.

*Experimental.*—At the suggestion of Prof. A. B. Cordley, of the Entomological Department, a chemical study was taken up at this station with the view of obtaining a wider knowledge of the nature and composition of lime-sulfur spray solution. At the outset it became evident that some additional analytical methods must be devised which would enable us to ascertain more definitely the nature and composition of the polysulfid and also to estimate the calcium hydroxide which might be present.

It is a well-known fact that when an acid is added to a metallic polysulfid, sulfur equivalent to form the monosulfid of the metal is liberated as hydrogen sulfid, while the remainder of the sulfur is deposited as free sulfur, *e. g.*:



For the sake of convenience, the sulfur equivalent to form the monosulfid is here spoken of as "sulfid" sulfur, while the remainder is spoken of as "polysulfid" sulfur. It can be readily seen that when the amount of "sulfid" and "polysulfid" sulfur are known the simplest formula of the polysulfid can be easily calculated.

*Method for "Polysulfid" Sulfur.*<sup>1</sup>—Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. For analysis 10 cc. aliquots are used. The aliquot is placed in a small beaker and about 30 cc. of distilled water is added. Tenth-normal hydrochloric acid is then run from a burette into the solution, drop by drop, with constant stirring until the yellow tint has practically disappeared. Two drops of methyl orange indicator is then added and the addition of the acid continued until the first permanent pink tint appears. (After standing for some time this tint will gradually disappear.) The solution will be milky white from the finely divided sulfur present, but it is not difficult to ascertain the exact end point of the reaction. After the solution is allowed to stand a few moments to permit the sulfur to settle and collect together, the sulfur may then be filtered on a weighed gooch crucible, thoroughly washed, dried at a low temperature (about 40°) and weighed directly as free sulfur. It has been found somewhat more accurate to filter the sulfur on a small filter paper and, after thoroughly washing, gently boil the paper and its contents in 50 cc. of 10 per cent. potassium hydroxide solution until all the sulfur is dissolved. Upon cooling, 50 cc. of a 3 per cent. solution of hydrogen peroxide free from sulfates is added. Heat on the steam bath for exactly 30 minutes and then acidify with hydrochloric acid, precipitate with barium chloride in the usual manner in boiling solution, and finally weigh as barium sulfate.

The precipitation of the sulfur by means of the weak acid does not decompose the thiosulfate in solution.

*Method for "Sulfid" Sulfur.*—For the determination of "sulfid" sulfur a well-known analytical method<sup>2</sup> has been but slightly modified. However, because of the manner of manipulation, it is deemed advisable to give it in detail. As it is used here, the zinc is not precipitated as the normal sulfid, but as the polysulfid.

An ammoniacal zinc chloride solution is prepared by dissolving 3.253 grams of pure zinc (or 4.0488 grams of pure zinc oxide is somewhat more convenient for use) in hydrochloric acid, supersaturating with ammonia and diluting to 1 liter. Each cc. of the solution is equivalent to 0.0016 grams of sulfur, or, in other words, it is a decimal normal solution.

<sup>1</sup> Bull. 76, Washington Station.

<sup>2</sup> J. Am. Chem. Soc., 1908, page 63.

<sup>3</sup> Circ. No. 1, Virginia State Crop Commission.

<sup>4</sup> Bull. 116, Massachusetts Experiment Station.

<sup>1</sup> The methods here given for "polysulfid" and "sulfid" sulfur do not involve any new principle. They are specially adapted to the conditions involved and have been found to be simple and accurate.

<sup>2</sup> Sultón's Vol. Analysis, Ninth Edition, page 325.

Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. Use 10 cc. aliquots for analysis. The zinc solution is run in from a burette until the filtered solution is colorless and no dark color is shown when a drop is brought in contact with an almost saturated solution of nickel sulfate spread in drops on a white porcelain tile. This titration will give the approximate end-point of the reaction. Several aliquots (four or five) are then placed in beakers and a series of determinations made by adding to the first the exact amount of zinc solution required in the above titration; to the second add 0.2 cc. less of the zinc solution; to the third, 0.4 cc. less, and so on. These should be then allowed to stand about 30 minutes to insure complete precipitation of the zinc. The aliquots are then filtered. The amount of zinc solution which just suf-

The final titrations with the zinc solution in this determination should be made on 20 cc. aliquots.

*Results of Analyses.*—The analytical methods devised by Haywood<sup>1</sup> and Avery<sup>2</sup> have been used somewhat extensively during this investigation and have been found to be quite satisfactory. Some of the analyses made by the use of Haywood and Avery's methods in conjunction with our own are given in Table I. The solutions are representative, consisting of commercial samples, together with samples prepared in the laboratory by the use of different formulas and having different concentrations. Many other analyses have been made, but the general relationships found were the same as in those here recorded and the analytical data are omitted to economize space. The results are calculated as grams per 100 cc. solution.

TABLE I.

Grams per 100 cc. original solution

No.	History of sample.	Total CaO.	Sulfid sulfur.	Polysulfid sulfur.	Thio- sulfate sulfur.	Sulfite and sulfate sulfur.	Calcium hydroxide.
1.	Commercial sample "Rex" lime-sulfur spray.....	12.12	5.92	23.06	1.47	0.08	None
2.	Commercial sample mfgd. by Oregon Spray & Gas Co., Portland, Oregon.....	12.86	7.04	25.30	1.78	0.12	None
3.	Commercial sample mfgd. by Niagara Spray Co., Hood River, Or.	12.38	6.79	23.90	0.82	0.08	None
4.	Laboratory sample made by boiling 55 grams CaO, 110 gram sulfur, and 400 cc. of water under reflux condenser for 1 1/4 hours.....	9.49	3.93	14.82	2.98	None	None
5.	Laboratory sample made by boiling 55 grams CaO, 55 grams of sulfur, and 450 cc. of water under reflux condenser 1 hour.	4.99	1.80	6.25	2.43	None	Trace
6.	Laboratory sample made by boiling 60 grams CaO, 110 grams sulfur, and 450 cc. water under reflux condenser 1 hour....	9.45	3.60	12.43	3.84	None	None

fices to remove all of the yellow color so that the resulting filtrate is colorless, is the correct titration. The great tinctorial power of the polysulfid serves adequately as an indicator in this determination.

The writers have been able to attain an accuracy of within 0.2 cc., or 0.0003 gram of sulfur, which is as close as could be determined gravimetrically.

For greater accuracy larger aliquots (say 20 cc.) may be taken for the final titrations.

*Method for Calcium Hydroxide.*—Attempts have been made to devise a method for the direct determination of the hydroxide by the use of a copper or zinc salt as suggested by Bloxam<sup>1</sup> in his work on ammonium polysulfids. None of these have been successful.

The amount of calcium hydroxide in the lime-sulfur solution may be calculated, however, from the data obtained in the above-described methods for the determination of "polysulfid" and "sulfid" sulfur. The amount of tenth-normal acid used in the precipitation of the sulfur in the first method is the amount necessary to react with both the polysulfid and the hydroxide present, while the number of cc. of zinc solution used in the "sulfid" sulfur method is the decinormal titration of the polysulfid only. The difference between the two titrations will represent the amount of tenth-normal acid required to neutralize the hydroxide.

The laboratory samples were made by boiling the stated length of time, then allowed to cool, and after standing 12 hours, the clear supernatant liquid was drawn off into glass-stoppered bottles. Upon standing a day or two longer the analyses were made. In the case of samples No. 5 and No. 6, orange-red, needle-shaped crystals separated out of the solution. A considerable excess of lime was used in the preparation of No. 5, and a slight excess in No. 6, and the crystals formed were undoubtedly the oxysulfids of calcium. These compounds seem to be of variable composition, as they have been stated by various investigators to be  $3\text{CaO} \cdot \text{CaS}_4 \cdot 12\text{H}_2\text{O}$ ,  $2\text{CaO} \cdot \text{CaS}_5 \cdot 10$  or  $11\text{H}_2\text{O}$ ,  $5\text{CaO} \cdot \text{CaS}_6 \cdot 20\text{H}_2\text{O}$ ,  $4\text{CaO} \cdot \text{CaS}_7 \cdot 18\text{H}_2\text{O}$ , or  $3\text{CaO} \cdot \text{CaS}_8 \cdot 14$  or  $15\text{H}_2\text{O}$ .

The amount of calcium hydroxide in the clear spray solution is only a trace, if any. It appears that if there is hydroxide in the freshly prepared solution it either unites with some of the sulfur already in combination to form more polysulfid, or it unites directly with the polysulfids to form oxysulfids which crystallize out of the more concentrated solutions.

The spray solution is always alkaline. Its alkalinity must be due to the hydrolysis of the polysulfid as the thiosulfate is not hydrolyzed to any extent. Küster and Heberlein<sup>3</sup> have found the sodium poly-

<sup>1</sup> Jour. Amer. Chem. Soc., 1905, page 244.

<sup>2</sup> Bull. 90, Bureau of Chemistry.

<sup>3</sup> Zeit. anorg. Chem., 1905, page 53.

<sup>1</sup> Jour. Chem. Soc., 1895, page 289.

sulfids to be strongly hydrolyzed in solution. The case of calcium polysulfid is analogous.

From Table I we are able to get an idea of the polysulfid. Thatcher<sup>1</sup> has stated unreservedly that the polysulfid is the pentasulfid. If this were correct, the amount of "polysulfid" sulfur would be exactly four times that of the "sulfid" sulfur. In nearly every instance our results show that the "polysulfid" sulfur is approximately  $3\frac{1}{2}$  times the amount of the "sulfid" sulfur, proving that the polysulfid in solution is not one compound only, but probably a mixture of the tetrasulfid and the pentasulfid of calcium.

*The Absence of the Hydrosulfid.*—In order to thoroughly establish the above given "sulfid" sulfur method and tabulated results it is necessary that the absence of the hydrosulfid should be proven. Wellington<sup>2</sup> and others have suggested the presence of this compound.

Divers and Shimidzu<sup>3</sup> showed that calcium hydrosulfid reacts very rapidly with sulfur to form polysulfid and liberate hydrogen sulfid, the action being as brisk as that of a strong acid with marble. When a solution of the hydrosulfid is heated with sulfur on a water bath the reaction is complete, only a trace of hydrosulfid remaining. Since free sulfur is always present in the preparation of lime-sulfur solution, it seems not probable<sup>4</sup> that the hydrosulfid could be present in appreciable quantity.

Divers and Shimidzu<sup>4</sup> employed a manganous salt for the detection of basylous hydrogen, the test being based upon the following reaction:  $\text{Ca}(\text{SH})_2 + \text{MnSO}_4 = \text{CaSO}_4 + \text{MnS} + \text{H}_2\text{S}$ , half of the sulfur present being liberated as hydrogen sulfid. Similar tests on the lime-sulfur solution with manganese sulfate have failed to reveal the presence of any hydrosulfid.

Again, when the spray solution is dried in hydrogen over sulfuric acid, hydrogen sulfid would be liberated by the decomposition of any hydrosulfid which might be present. Only the merest trace of hydrogen sulfid has been found to be liberated under these conditions.

In the "sulfid" sulfur determination, any hydrosulfid would in all probability be precipitated as zinc hydrosulfid and, since it is calculated as the normal sulfid only one-half of the sulfur present as hydrosulfid would be shown by the titration with the zinc solution. A comparison of the amount of "sulfid" sulfur found by this method with the amount of sulfur which could be liberated from the solution as hydrogen sulfid was made. The determination of the hydrogen sulfid was effected by adding exactly enough tenth-normal acid to completely react with the sulfids present and passing the gas liberated into

an ammoniacal zinc chloride solution. The zinc sulfid thus obtained was digested in a small amount of concentrated potassium hydroxide solution, oxidized with hydrogen peroxide, and precipitated in the usual manner as barium sulfate. The comparative results of one of the determinations made in this way are as follows:

By "sulfid" sulfur method, 3.42 grams sulfur per 100 cc.

Sulfur liberated as  $\text{H}_2\text{S}$ , 3.44 grams sulfur per 100 cc.

If the hydrosulfid were present in any quantity there would be an appreciable difference found in the amounts of sulfur obtained by the two different methods. No such difference has been found in the determinations made.

From the above data it may be said that only a trace of hydrosulfid, if any, is present in the lime-sulfur solution. What little there may be is perhaps that which might be formed by the hydrolysis of the polysulfid.

*The Nature of the Polysulfid.*—When the spray solution is brought in contact with benzene or with chloroform sulfur is extracted in considerable amount. This fact led to a rather extended study of the polysulfids, for it seemed that some of the sulfur was held in very feeble combination if not in physical solution. An endeavor was made to ascertain just the exact amount of sulfur which could be extracted from a definite quantity of the spray solution. Preliminary tests showed that carbon disulfid cannot be used for making such an extraction because it reacts rapidly with the polysulfid to form a thiocarbonate.

Small quantities (5 and 10 cc.) of the solution were shaken in separatory funnels with benzene and with chloroform, the solvent in each instance being removed occasionally and new quantities added. The combined extractions made by the two solvents respectively were then distilled and the residual sulfur determined. A considerable quantity of sulfur was obtained from both the chloroform and the benzene extraction. However, a definite end-point to the extraction could not be obtained, for even after several days' extraction some sulfur continued to be gradually dissolved. Upon investigation it was found that during the extraction an oxidation of some of polysulfid to the thiosulfate had occurred, due to the contact with air in the separatory funnel, and some of the free sulfur was constantly liberated by this reaction. A very small amount of calcium carbonate was formed from the carbon dioxide present.

An extraction apparatus similar to that devised by A. H. Fiske<sup>1</sup> was arranged so that a quantity of the lime-sulfur solution could be extracted with benzene without coming in contact with the air. An ex-

<sup>1</sup> *Trans. Amer. Chem. Soc.*, **1906**, page 63.

<sup>2</sup> *Bull.* **116**, Mass. Exp. Station.

<sup>3</sup> *Ind. Chem. Soc.*, **1894**, page 270.

<sup>4</sup> *Ind. Chem.*

<sup>1</sup> *Amer. Chem. Jour.*, **41**, page 510.



traction was made using 10 cc. of lime-sulfur solution. At the beginning a much larger quantity of sulfur was extracted than near the close of the experiment, which required several days' time. A definite end-point to the extraction could not be obtained and an examination of the extracted solution showed that there had been a considerable increase in the amount of thiosulfate, besides the formation of a very small quantity of what appeared to be calcium carbonate. The experiment was repeated, using 5 cc. of lime-sulfur solution diluted with 5 cc. of water. The details were carried out much more carefully than in the previous trial, but the results were the same. It was evident that either the benzene absorbed enough oxygen and carbon dioxide from the air in the apparatus to effect the composition of the solution, or else there had been a decomposition of the polysulfid with the formation of more thiosulfate as well as small amounts of other products.

Previous to the benzene extraction described above, an attempt was made to evaporate some of the lime-sulfur solution in partial vacuo, extract the dried residue with some sulfur solvent and ascertain what definite polysulfid, if any, remained. An experiment was tried drying 10 cc. of the solution in partial vacuo over calcium chloride. The quantity of thiosulfate increased enormously during the evaporation, indicating that an oxidation of the polysulfid had taken place.

Drying the solution in hydrogen sulfid was next tried, but the gas reacted rapidly with the solution, precipitating sulphur and forming hydrosulfid of calcium.

It was found after many trials that the solution could be successfully evaporated in pure hydrogen over sulfuric acid. Because of the conflicting data on the polysulfids in general, the details of the following experiments are given quite fully:

A lime-sulfur solution was made by boiling 55 grams of calcium oxide, 110 grams of sulfur and 450 cc. of water under a reflux condenser for one hour. Pure hydrogen was prepared from pure zinc and dilute sulfuric acid and washed, first with a potassium permanganate solution, then with a saturated solution of mercuric chloride, and finally with a strong solution of potassium hydroxide. The hydrogen was dried by passing it first through a calcium chloride tube and then through sulfuric acid.

Ten cc. of the lime-sulfur solution was placed in each of three glass mortars, which were immediately placed over sulfuric acid in different desiccators, and hydrogen passed into each until all traces of air were removed. The desiccators were then stoppered tightly, placed in a dark room where the temperature did not rise above 16°, and the solutions allowed to dry for three weeks. During this time the sulfuric acid became slightly turbid, indicating that a trace

of hydrogen sulfid had been liberated. The dried residues had a light yellow color and contained some crystals of thiosulfate. Before opening the desiccators the hydrogen in them was tested and found to be practically pure. The dried residues were then removed, one by one, and immediately covered with pure, freshly distilled, dry carbon disulfid, previous tests having shown that this substance does not react with the dried material. The residues were ground to a fine powder while still under the solvent. The carbon disulfid was then decanted off and the residues carefully washed with a fresh supply. That a considerable amount of free sulphur was extracted was certain from the yellow color of the solvent after the extraction. The powdered residues were then transferred to wide-mouthed glass-stoppered bottles and covered with more carbon disulfid. Long standing failed to extract any more sulfur. After the solvent was decanted off the residues were dried in a current of hydrogen and then analyzed. The analyses of the residues and the original material are given in Table II, the results being calculated as grams per 100 cc. original solution:

TABLE II.  
Grams per 100 cc. of original solution

No.	Sample.	Total CaO.	Thio- sulfate sulfur.	Poly- sulfid sulfur.	Sulfate and sulfite sulfur.	Sulfur extracted with CS <sub>2</sub> .
1.	Original solution...	9.68	3.39	15.05	3.85	None
2.	Dried residue.....	9.25	3.43	3.64	3.58	11.25
3.	Dried residue.....	9.52	3.71	3.82	3.72	11.21
4.	Dried residue.....	Lost	3.84	4.43	3.60	10.28

The above-described experiment was repeated, using a lime-sulfur solution made by boiling 60 grams of lime, 110 grams of sulfur, and 450 cc of water under a reflux condenser for 2½ hours. The method of procedure was the same with the exception that a fresh supply of hydrogen was passed into the desiccator every day or two in order to keep the supply pure and also to remove all traces of hydrogen sulfid which might be liberated. The results, calculated as grams per 100 cc. original solution are given in Table III:

TABLE III.  
Grams per 100 cc. original solution.

Sample.	Total CaO.	Thio- sulfate sulfur.	Poly- sulfid sulfur.	Sulfite and sulfate sulfur.	Sulfur extracted with CS <sub>2</sub> .
Original solution.....	8.24	1.41	14.71	4.16	None
Dried residue	8.11	1.76	3.70	4.00	None 11.05

From the results given it appears that there is a more stable, primary polysulfid of calcium. Although the analyses given do not permit of a definite statement regarding its composition, it does correspond, however, very closely to the formula CaS<sub>2</sub>. The slight variability in the results obtained may be

<sup>1</sup> A small amount of residue No. 2 was lost after the extraction with carbon disulfid had been made, hence the low results on lime, etc.

due to the fact that some of the higher polysulfid may not have been entirely decomposed in some instances. The writers have not found any indication whatsoever of the presence of the monosulfid in the dried residue.

Other investigators have found similar cases. Bloxam<sup>1</sup> discovered that of the potassium polysulfids, there was a more stable one having the formula  $K_2S_8$ . Küster,<sup>2</sup> in his work on the sodium polysulfids, found that after the polysulfid  $Na_2S_4$  is formed the remainder of the sulfur in solution is not so firmly combined.

This lower primary polysulfid of calcium is amorphous, and mustard-yellow in color. It is readily soluble in water and 95 per cent. alcohol. When dry it is stable in the air.

An attempt was made to separate the polysulfid from the thiosulfate in the dried residue by the use of a solvent which would dissolve only the polysulfid. Trials were made using 80 per cent., 90 per cent., 95 per cent. and 98 per cent. alcohol, respectively, as the solvent, but the thiosulfate was found to be somewhat soluble even in 98 per cent. alcohol. The polysulfid is not soluble in absolute alcohol. No solvent has been found which will effect the complete separation of the thiosulfate from the polysulfid. All efforts to prepare a pure solution of calcium polysulfid from which a residue free from thiosulfate might be obtained have been unsuccessful, some thiosulfate being always present, though in some instances in very small amount.

Viewed in the light of previous investigations, it seems evident that all of the sulfur found in the lime-sulfur solution must be in chemical combination. The latest extensive work on this question was done by Küster and Heberlein on the sodium polysulfids.<sup>3</sup> These investigators state that the polysulfids are analogous to the polyiodides and are the salts of hydrogen sulfid acids of the formula  $H_2S_x$ . They found that the more sulfur there is present, the less the hydrolysis of the polysulfid. This fact is indicative of chemical combination, for, if after a certain definite polysulfid is formed the remainder of the sulfur is simply in physical solution, there would be but little change in the amount of hydrolysis after enough sulfur had been added to form the primary compound.

These experiments with the polysulfid reveal a fact of practical significance in regard to the spray solution. It is not necessary for the polysulfid to oxidize in order that free sulfur be deposited, as has heretofore been stated. If the polysulfid is not oxidized completely before the spray dries on the tree, there will be left a lower polysulfid and some sulfur will be deposited, which is not the result of oxidation.

A considerable amount of the sulfur in lime-sulfur solution is in very feeble combination and for the practical purposes to which it is applied might be considered as sulfur in physical solution.

*Effect of Time of Boiling.*—Previous work on the lime-sulfur spray has shown that one hour is sufficient time for boiling in the preparation of the solution. Prolonged boiling has been found not to effect materially its composition. This latter statement has been found by us to be true only for certain conditions.

Solutions were prepared using different formulas and different lengths of time for boiling. The cookings were made under a reflux condenser and the samples were analyzed after standing 24 hours. The results calculated as grams per 100 cc. original solution are given in Table IV:

TABLE IV.  
Grams per 100 cc. original solution.

No.	History of sample.	Total CaO.	Sulfid sulfur.	Poly- sulfid sulfur.	Thio- sulfate sulfur.	Sulfate and sulfite sulfur.
1.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. of water for one hour.....	5.15	1.84	6.49	2.43	Trace
2.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. water for 2 1/2 hours	5.10	1.82	6.32	2.45	Trace
3.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 1 hour....	9.45	3.60	12.43	3.84	Trace
4.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 2 1/2 hours	8.39	4.16	14.71	1.40	Trace

In the case of samples No. 1 and No. 2, prolonged boiling did not effect the composition of the spray. With No. 3 and No. 4, where a larger proportion of sulfur was used, there was, however, a decided decrease in the amount of thiosulfate and an increase in the polysulfid present. There was also less lime in the solution. These results indicate that when the sulfur used is approximately double the quantity of lime, continued boiling does exercise a much more marked effect on the composition than when equal parts of lime and sulfur are used. The writers have been unable to furnish a complete, satisfactory explanation for the occurrence of this phenomenon. It may be said, however, that when the clear lime-sulfur solution is boiled hydrogen sulfid is liberated in considerable quantity, because of the hydrolysis of the polysulfid. As the hydrogen sulfid is liberated a deposit of calcium sulfite is obtained. The formation of the sulfite is due, no doubt, to the decomposition of the thiosulfate in the boiling solution.

*Effect of Carbon Dioxide on the Lime-sulfur Solution.*—It has been conjectured by some that the carbon dioxide of the atmosphere may have an influence in the decomposition of the diluted lime-sulfur solution when sprayed upon the tree. Some

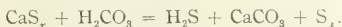
<sup>1</sup> Jour. Chem. Soc., 1900, p. 753.

<sup>2</sup> Zeit. anorg. Chem., 1905, p. 53.

<sup>3</sup> Ibid., 1905, p. 53.

work has been done by the writers to test out this point.

Pure carbon dioxide was passed into some of the concentrated lime-sulfur solution. A large quantity of hydrogen sulfid was rapidly liberated; apparently as much as if some strong acid were used. The following reaction occurs:



Two experiments were made by passing air through first a dilute lime-sulfur solution and then through a 10 per cent. solution of copper sulfate. Any hydrogen sulfid liberated would react to form copper sulfid in the latter solution. The air was passed through until the dilute spray solution no longer possessed a yellow color, the polysulfids present being completely decomposed. In one instance the air was used directly and in the other the carbon dioxide was removed by passing through a potassium hydroxide solution.

There was a distinct precipitate formed where the normal amount of carbon dioxide was present. However, the precipitate was quite small. The decomposed lime-sulfur solution had a strong odor of hydrogen sulfid. Paper moistened with lead acetate solution was gradually darkened, showing the presence of the gas.

In the instance where the air free from carbon dioxide was used there was only a trace of copper sulfid precipitated. The decomposed lime-sulfur solution had an odor of hydrogen sulfid. Evidently some hydrogen sulfid is formed during the oxidation, whether carbon dioxide is present or not, probably due to the hydrolysis of the polysulfid. The solution decomposed more rapidly when carbon dioxide was present, showing that it does exercise an influence in the decomposition of the spray, but our results indicate that this influence is comparatively small. The presence of hydrogen sulfid should not be overlooked in the consideration of the immediate insecticidal value of the spray.

In conclusion, it may be said that the above results are presented as derived from a limited study made in this laboratory, and with a full realization that the lime-sulfur solution is a complex equilibrium subject to the influence of many varying conditions.

*Summary.*—1. Simple and accurate methods for the determination of the composition of the polysulfids and the amount of calcium hydroxide have been perfected.

2. Free dissolved calcium hydroxide is not a constituent of the lime-sulfur solution, its alkalinity being due to the hydrolysis of the polysulfid.

3. The polysulfids in the solution are probably a mixture of the tetrasulfid and pentasulfid of calcium.

4. Our tests show the absence of appreciable quantities of hydrosulfid. Should any be present, it is

that which might be formed by the hydrolysis of the polysulfid.

5. There seems to be a more stable polysulfid of calcium which our results indicate to be  $\text{CaS}_2$ . A considerable amount of the sulfur in the solution is very feebly combined and for practical spraying purposes may be considered as sulfur in physical solution.

6. It is not necessary for the spray to oxidize in order that free sulfur may be deposited from the same.

7. Prolonged boiling when approximately one part of lime to two parts of sulfur are used causes an increase in the amount of polysulfids and a decrease of thiosulfate.

8. Carbon dioxide reacts with the lime-sulfur solution, liberating hydrogen sulfid. Our laboratory experiments indicate that the carbon dioxide of the air exercises some influence in the decomposition of the spray upon the tree.

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[CONTRIBUTION FROM THE LABORATORY OF THE HAWAII EXPERIMENT STATION. PAPER No. 2.]

## THE AVAILABILITY OF SOIL PHOSPHATES.

By W. P. KELLEY.

Some time after the announcement of the "Mineral Theory" of agriculture by Liebig, it began to be recognized that, while absolute analyses of soils are of value in agricultural practices, the larger part of the mineral substances of the soil is in a state in which it cannot be absorbed by most plants. The recognition of this fact has led to the development of a number of methods for the determination of the so-called available plant foods of the soil. It is generally considered that substances, available for plant growth, must either be in solution in the soil moisture or readily soluble in the secretions from root surfaces. Other factors, such as the physics and biology of the soil, play an important part in the question of fertility, however, and unless due consideration is given these factors entirely erroneous conclusions may be drawn from solubility determinations. Nevertheless, any step which leads to a knowledge of the state of solubility of the substances in the soil is an important one.

While some attention has been given to the determination of available plant foods in general, by far the larger part of these investigations has dealt with the phosphates. Some years ago the Association of Official Agricultural Chemists adopted the use of N/5 hydrochloric acid for the determination of the more active forms of  $\text{P}_2\text{O}_5$ . In this determination 200 grams of soil are digested with 2000 cc. of N/5 hydrochloric acid at  $40^\circ$  for five hours, due allowances



being made for the neutralization of the acid by soil carbonates, etc. More recently some chemists have substituted N/5 nitric<sup>1</sup> acid in this determination. In the publications bearing on this point but little field data has been submitted,<sup>2</sup> and therefore the reader is left with uncertainty as to whether or not the results given are of purely theoretical importance. No one claims, however, to be able to imitate natural conditions and extract from the soil the plant food that is immediately accessible to growing crops. The availability probably depends on the rate of solubility as much as on the absolute amount dissolved at any one time. On the contrary, it is only hoped to secure results of comparative value.

In the course of some investigations at the Indiana Experiment Station, the author had occasion to compare both the official and the nitric acid methods in the determination of available phosphates in a large number of soils in Indiana on which field experiments had been conducted. Some of these showed a response to the application of phosphatic fertilization; others did not. The following table,<sup>3</sup> selected from a large number of these determinations, shows the total  $P_2O_5$  and the percentage soluble in N/5 hydrochloric and nitric acids, respectively.

TABLE I. TOTAL  $P_2O_5$  IN INDIANA SOILS, AND PERCENTAGE SOLUBLE IN N/5 ACIDS.

Soil No.	Description of soil.	Total $P_2O_5$ Per cent.	$P_2O_5$ sol- uble in N/5 HCl		$P_2O_5$ sol- uble in N/5 HNO <sub>3</sub>	
			Per cent.	Per cent.	Per cent.	Per cent.
1.	Gray silt loam.....	0.08	0.0050	0.0060		
2.	Gray silt loam.....	0.08	0.0030	0.0025		
3.	Yellow silt loam.....	0.13	0.0028	0.0034		
4.	Brown silt loam.....	0.11	0.0016	0.0022		
5.	Sandy loam.....	0.10	0.0080	0.0078		
6.	Dark sandy loam.....	0.20	0.0008			
7.	Peaty soil.....	0.34	0.0380	0.0360		
8.	Peaty soil.....	0.40	0.0800	0.0830		

The above table shows that the solubility of the phosphates in these soils varies between very wide extremes, and that the differences between the solubility in N/5 hydrochloric and nitric acids are too slight to be of any consequence. On these various soils field experiments, involving the use of phosphates, etc., have been conducted for many years. Various crops have been grown, although the principal ones are corn and wheat. The following table shows the solubility of the soil phosphates in N/5 hydrochloric acid, and the effects on the yield of certain crops brought about by the application of phosphate. While it is true that the application of any given fertilizer does not always produce the same effects in different seasons, the data submitted fairly represents the action of phosphate on these soils.

<sup>1</sup> Peter and Averett, *Bull.* 126, Ky. Expt. Sta.; Whitson and Stoddard, *Research Bull.*, No. 2, Wisc. Expt. Sta. Snider, *Bull.* 102, Minn. Expt. Sta.

<sup>2</sup> Snider gives some data bearing on this point; also Fraps gives some results from pot experiments in an article entitled "Availability of Phosphoric Acid in the Soil," *Jour. Am. Chem. Soc.*, 28, 824.

<sup>3</sup> This data is taken from a thesis for a Master's degree presented to Purdue University in 1907, and published by permission.

<sup>4</sup> Not determined.

TABLE II. PERCENTAGE OF  $P_2O_5$  SOLUBLE IN N/5 HYDROCHLORIC ACID AND THE EFFECTS OF THE APPLICATION OF PHOSPHATE UNDER FIELD CONDITIONS.

Soil No.	$P_2O_5$ sol- uble in N/5 HCl		Crop grown.	Effects of the application of phosphate.
	Per cent.	Per cent.		
1.	0.0050		Corn	Yield increased 10 bu. per acre
2.	0.0030		Wheat	Yield increased 5 bu. per acre
3.	0.0028		Potatoes	Yield increased 50 bu. per acre
4.	0.0016		Corn	Yield increased 14 bu. per acre
5.	0.0080		Corn	Yield increased 6 bu. per acre
6.	0.0605		Corn	No increase
7.	0.0380		Corn	No increase
8.	0.0800		Corn	No increase

In all these soils, except the sandy loam and peaty soils, we find that the application of phosphate produced an increase in the growth of the crop in question. The total  $P_2O_5$  in the sandy loam and peats is considerably greater than in the other types, but the percentage dissolved in N/5 hydrochloric acid is likewise very much greater. With but few exceptions, the soils of Indiana that contain less than 0.01 per cent.  $P_2O_5$ , soluble in N/5 hydrochloric acid, are benefited by the application of soluble phosphate, and seldom do those containing more than this amount respond to its application.

In order to maintain a strictly N/5 acid solution in the determination of available phosphate it is necessary to determine the amount of acid the soil is capable of neutralizing under the same conditions that are employed in the actual determination of the soluble phosphate. Some soils contain large amounts of carbonates; others do not, and if the phosphate solubilities are comparable, they must be made by the use of the same strength solvent. In the preliminary digestion for the determination of this neutralizing power it was noticed that those soils which neutralized a large amount of acid contained a correspondingly large percentage of soluble  $P_2O_5$ , whereas, soils having a slight neutralizing power were found to contain a small percentage. For a number of years soils that neutralized but little acid in the preliminary digestion have been considered as being in need of lime, since it is generally accepted that the presence of carbonate of lime promotes bacterial activity, as well as neutralizes soil acidity. The following table will show the neutralizing power of these soils and the percentage of  $P_2O_5$  soluble in N/5 hydrochloric acid:

TABLE III. THE N/5 HCl NEUTRALIZED BY ONE GRAM OF SOIL, AND THE PERCENTAGE OF AVAILABLE  $P_2O_5$ .

Soil No.	Acid neutralized cc.	$P_2O_5$ soluble in N/5 HCl. Per cent.
1.	0.37	0.0050
2.	0.25	0.0030
3.	0.50	0.0028
4.	0.50	0.0016
5.	0.44	0.0080
6.		0.0605
7.	3.87	0.0380
8.	6.00	0.0800
9.	4.00	0.0420

Not recorded.

The above table shows that a low solubility of phosphates is associated with a slight neutralizing power in the soil; and that there is a casual relation between the absence of active bases, on the one hand, and the low solubility of phosphates, on the other, seems likely. Whitson and Stoddard<sup>1</sup> have recently pointed out that acid soils in Wisconsin need phosphates. In Indiana the same conditions prevail.

The author recently pointed out that while the litmus test for soil acidity is unreliable,<sup>2</sup> the amount of N/5 hydrochloric acid which the soil is capable of neutralizing offers a very trustworthy indication of the needs of lime, and while the neutralization factor gives valuable indication of the need of lime, it is also very useful as a rapid means of determining phosphate deficiencies;—not that it could be relied upon as a definite indication, but is valuable as a suggestion. The fact that the N/5 hydrochloric acid method gives reliable indications concerning the application of phosphates, with such soils as prevail in the central west, led to an inquiry concerning its applicability to the soils of Hawaii, which are of a vastly different origin and type.

The entire island group of Hawaii is of volcanic origin, and from a geological standpoint, of a recent formation. The soils of Hawaii, being very largely derived from disintegrated basaltic lava, are characterized by a very high percentage of iron and alumina, and a relatively small percentage of calcium. As an average of a large number of determinations, these soils have been found to contain about 40 per cent. iron oxide and alumina, soluble in concentrated hydrochloric acid, whereas the combined iron and alumina of American soils probably do not exceed 6 per cent. In this investigation it was thought well to compare the solubility in both N/5 hydrochloric and nitric acids. The following table will show the results:

TABLE IV. HAWAIIAN SOILS, SHOWING SOLUBILITY OF PHOSPHATES.

Soil No.	Total. Per cent.	Soluble in N/5 HCl. Per cent.	Soluble in N/5 HNO <sub>3</sub> . Per cent.	Acid neutralized by one gram soil. cc.
10	0.07	Trace	Trace	0.90
11	0.35	Trace	Trace	1.80
12	0.20	Trace	Trace	1.30
13	0.55	0.1128	0.1025	3.50

Soils Nos. 10, 11 and 12 are found to contain only a trace of soluble  $P_2O_5$ , being, in each instance, not more than 0.0005 per cent., while No. 13 contains a very large percentage of available phosphate. The first three samples are representative of the upland soils of Oahu, having been taken from an elevation of 650 feet or more. Soil No. 11 is highly manganeseiferous. Each of these has been derived from primary lava. No. 31, however, is a coast-wise soil, derived from the disintegration of volcanic ash and cinders, having been subsequently submerged by the sea,

during which time a considerable portion of coral limestone was incorporated with what is now the soil. Just as with the Indiana soils, we find that the neutralization coefficient bears a direct relation to the state of solubility of the phosphate.

It has been considered for some time that calcium phosphate is available for plant growth, whereas the basic phosphates of iron and alumina are not. Some years ago Fraps<sup>1</sup> pointed out that the solubility of the basic phosphates of iron and alumina in N/5 hydrochloric and nitric acids is very slight, whereas the solubility of calcium phosphate is complete. The Wisconsin investigators have recently shown that soils which respond to the application of phosphates contain not only a much smaller percentage of  $P_2O_5$  soluble in N/5 nitric acid but also relatively more of the basic phosphates of iron and alumina than do the soils which do not respond to the application of phosphate.

While N/5 hydrochloric acid has been shown to completely dissolve calcium phosphate, and to effect only a slight solution of the basic phosphates of iron and alumina, Stoddard<sup>2</sup> points out that a one per cent. solution of sodium hydroxide is capable of dissolving the basic phosphates of iron and alumina while possessing only a slight solvent power for calcium phosphate. With soils that contain such large percentages of iron and alumina as prevail in Hawaii, it seems likely that a correspondingly high percentage of the phosphates would be combined with these bases, and hence be unavailable for plant growth.

With a view of testing this point, 100 grams of air-dried soil were digested with 1000 cc. of a one per cent. sodium hydroxide solution at 40° for five hours; the solution filtered and the  $P_2O_5$  determined in the filtrate. For the sake of comparison, the solvent powers of N/5 hydrochloric acid and one per cent. sodium hydroxide are given; and also the effects of the application of phosphate:

TABLE V.—SHOWING THE  $P_2O_5$  DISSOLVED BY N/5 HCl AND 1 PER CENT NaOH FROM FERRUGINOUS SOILS.

Soil No.	Soluble in N/5 HCl. Per cent.	Soluble in 1 per cent. NaOH. Per cent.	Crop grown.	Effect of the application of phosphate. Per cent. increase.
10	Trace	0.0060	Pineapples	50
11	Trace	0.0219	Pineapples	100
12	Trace	0.0489	Cotton	200
13	0.1128	0.1858	Rice	No effects

The above results show that while these soils contain considerable  $P_2O_5$  as basic phosphates of iron and alumina, in the case of soil No. 13, there is also a large percentage of the phosphoric acid combined with calcium. These results show that the N/5 hydrochloric method is of value in determining phosphate deficiencies in soils of widely different types,

<sup>1</sup> *ibid.*<sup>2</sup> "Soil acidity in its relation to available phosphates." *Research Bull. No. 2*, Wis. Expt. Station.<sup>3</sup> Estimated.<sup>1</sup> *ibid.*<sup>2</sup> Soil Acidity, *Sugar Planter's Month.*, May, 1909.

although there is an indication that the strength of the acid is not sufficiently great for highly ferruginous soils.

It is generally considered that apatite (soluble in  $N/5$  HCl), and wavellite and duferinite (soluble in 1 per cent. NaOH solution), constitute the principal mineral phosphates of the soil (soil No. 10 may contain some triplite), and yet the combined  $P_2O_5$  dissolved by the two solvents, constitutes but a small percentage of the total phosphate in the soil. It is true that the dissolving power of a given solvent toward a pure chemical may be greatly modified when the same body is associated with numerous other substances, such as occur in soils. Furthermore, these soils contain a large percentage of finely divided ferric hydrate which so permeates and surrounds the soil particles that a complete dissolution can be brought about only by use of agents that are capable of dissolving the iron also.

It<sup>1</sup> has been suggested that the amount of  $P_2O_5$  recovered from a soil by the use of a given solvent is not a true measure of the dissolving power of this solvent towards the phosphates in the soil, since some of the  $P_2O_5$ , after being dissolved, is refixed by the soil. In this connection it has been shown that these soils possess a high fixing power for soluble phosphates. It seems more likely, however, that only a small percentage of the phosphates present was dissolved by the solvents employed.

We should expect soils which contain from ten to twenty times as much iron and alumina as calcium to hold the phosphoric acid, combined largely with iron and alumina, rather than calcium; and the behavior of crops on these soils, together with their solubility, indicates the correctness of this view.

[CHEMICAL LABORATORY, NORTH CAROLINA DEPARTMENT OF AGRICULTURE]

## A RAPID METHOD OF DETERMINING CRUDE FIBER.

By J. M. PICKEL

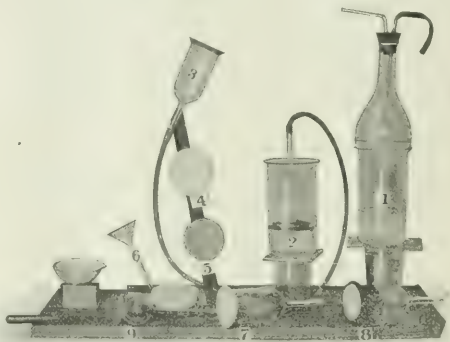
Received January 17, 1910.

This is, in the main, a method of filtering and washing the fiber. The filtration is effected by *upward* suction of the fiber against linen. The method was first used by the writer in the summer of 1902, since when it has been in constant use in this laboratory. A bare outline of the method was published in *Science* (Jan. 8, 1904).

Figure 1 (accompanying illustration) shows the manner of digesting the fiber: a beaker 7 to 8 cm. in diameter, about 15 cm. deep, capacity 600 to 800 cc., covered by a round-bottom flask through which flows cold water. Any convenient number of such diges-

ters may be connected in series by rubber tubes 25 to 30 cm. long, and the water run through the series from first flask to last. There is no loss of digesting liquid by evaporation; and if the boiling is started and conducted slowly, no great trouble from foaming, since each digester may, without disturbing its neighbor, be lifted and swirled.

Figures 3, 6, 7, 9 show suitable forms of filters—broad mouth tube, funnel, thistle tube—each provided with a rim or flange over which the linen disc is drawn taut. Convenient dimensions of these tubes (Figs. 3, 7) are, large end, diameter 5 to 6 cm., length 6 to 9 cm.; total length, including stem, 18" to



20 cm; diameter of stem, inside, about 0.5 cm. The rim or flange should be about 0.5 cm. wide, turned at nearly right angle to the axis of the tube or funnel and uniform in diameter. Note the rims (Figs. 3 and 6). The linen disc (Fig. 4) is attached to the tube by means of a strong, but not too coarse, flax thread. This thread is passed in short running stitches through the linen in a circle (Fig. 4) whose diameter is greater than that of the rim of the tube (or funnel), but not so much greater that, when the linen is drawn over the rim and the thread tied, it (the thread) will press against the side of the tube—the entire “pull” of the thread should be exerted on the linen. This adjustment is easily made once for all, and permanently fixed in the shape of a pasteboard (or metal) disc (Fig. 5) which shall serve as a pattern; any needlewoman can then make the linen discs by the score or hundred, according to need. As each linen will serve for a half dozen or more fiber determinations, these filters are inexpensive. In addition to the larger filter, 5 to 6 cm. diameter, a smaller one, diameter about 2.5 cm., is needed. A perforated disc (copper) over the mouth of the tube, under the linen, is useful but not indispensable.

*Operation.*—The filter having been connected by

<sup>1</sup> Pray, *Loc. cit.*



heavy rubber tube to a Bunsen suction pump and suction turned on, the surface of the filter is put in contact and kept in contact with the surface of the liquid in the beaker (Fig. 2) until all the liquid is drawn into the filter-tube, when the latter is withdrawn and reversed (Fig. 3) to permit the liquid to be sucked out. The suction is then discontinued, the fiber washed with 50 to 75 cc. of boiling water back into the beaker, stirred thoroughly, allowed, if need be, to subside a few moments, and the liquid sucked out through the filter, as above described. Three or four such washings will free the fiber of acid or alkali. When freed of acid, the fiber is washed back into the beaker with the requisite quantity of 1.25 per cent. alkali and digested. Finally, when filtered and washed (as above described) free of alkali, the fiber is washed with distilled water into a 50 cc. tared evaporation dish (royal Berlin porcelain in absence of platinum), the water evaporated on steam bath, the fiber dried, weighed, incinerated, the ash weighed, the fiber obtained by difference in the usual way. A small flexible steel spatula is often useful in removing the fiber from the linen and in bringing it into the dish. It will not infrequently happen that the dish will get full of water before all the fiber is washed into it; in such case, the excess of water is removed by suction through the small filter above referred to.

Experiments with filtering materials other than linen—hardened filter paper, flannel, chamois skin, unglazed porcelain discs (Fig. 8) were made—but the first and last are out of the question because of slowness, the two others are not suitable with hot alkali.

*Results Obtained by the Method.*—Duplicates on peanut hulls, corn bran, rice chaff, corn cobs, and peanut middlings gave results differing by 0.01 per cent., 0.14 per cent., 0.32 per cent., 0.20 per cent., 0.12 per cent., respectively. In the case of six samples of cocoas, duplicates were obtained differing by 0.02 per cent., 0.33 per cent., 0.03 per cent., 0.02 per cent., 0.06 per cent., 0.13 per cent. in each case. The fiber of cocoa, a fine powder, is one of the most difficult to filter and wash—next to impossible with a Gooch filter, but comparatively easy and quick by this method.

The filtrates and wash-water from the second or alkaline digestion were, after having passed through the linen filter, put through gooches (asbestos). It was found in six fiber determinations (wheat bran, shorts, cornmeal, "ship stuff") that the gooches retained 0.21 per cent. to 0.37 per cent. of solids, reckoned as fiber, that had passed through the linen; in the case of seven cocoas, filter paper (the hardened variety) retained 0.02 per cent., 0.02 per cent., 0.02

per cent., 0.26 per cent., 0.27 per cent., 0.35 per cent., 0.46 per cent., respectively, of solids which had passed through the linen.

The filtering (from the second or alkaline digestion), washing and transferring of the fiber to the evaporating dishes in the case of six cocoas consumed sixty-six minutes, an average of eleven minutes to the determination; the filtrates from these determinations were then put through hardened filter paper under suction, the shortest time of filtering in any of the six cases was one hour, the longest seven hours.

The above tests of the method were made several years ago. The author has hoped from year to year to make more extended and searching experiments, but has not been able to do so.

The official method of the U. S. Dept. of Agr. (Bur. of Chem., *Bull.* 107, p. 56, revised) for crude fiber says: "Filter through linen, asbestos or glasswool"—nothing as to particular grade of linen. One naturally selects, if linen, that of finest, closest mesh obtainable. Old filters of the author, still on hand, are 32 x 32 per square cm., that is, contain about thirty-two threads each way to the cm.; the threads are apparently about 0.2 to 0.3 mm. in diameter. Undoubtedly *standard*, or *better standardized* linen—if that material be finally found to be best—should be adopted.

There is a kind of felt, composed mainly of cotton, comparatively thin, uniform in texture; it would probably make an excellent filter. It is to be had at tailoring establishments.

RALEIGH, N. C., Jan. 10, 1910.

## THE DETERMINATION OF CRUDE FIBER.

By G. M. MACNIDER.

Received February 17, 1910.

In carrying out the method of the A. O. A. C. for the determination of crude fiber in cattle feeds<sup>1</sup> we have tried a good many modifications of the apparatus to shorten the time required and to make the determination less laborious. As the apparatus in use in this laboratory at present has proved satisfactory, some of the modifications in use may be of interest to chemists engaged in agricultural work.

The digestions with 1.25 per cent. sulphuric acid and 1.25 per cent. sodium hydroxide are done in 600 cc. Jena glass beakers, 16.5 cm. in height and with a uniform diameter of 8 cm. During the digestion a clock glass is placed over the beaker to condense the steam. This is fairly satisfactory, but considerable trouble is frequently caused by the frothing of the liquid, thereby necessitating the washing of the

<sup>1</sup> Bureau of Chemistry. *Bull.* No. 107 (revised).

substance from the sides of the beaker, and by the loss by evaporation which varies the strength of the solution. A number of different forms of condensers were tried to overcome both of these difficulties, but with only a fair amount of success. The author has found the following apparatus very satisfactory: this consists of an upright Liebig condenser, the lower end of which passes through a large rubber stopper which fits into the beaker described above. The stopper also carries a small tube for the introduction of a stream of air. (The use of a stream of air is suggested in the official method.) When the digestions were done in this apparatus it was found that with the use of only a weak stream of air the frothing even on the most difficult samples, *i. e.*, low-grade cottonseed-meals, could be so controlled that no error was introduced from this source. By using the Liebig condenser in place of a glass tube condenser or a flask containing water placed on the beaker there was so little loss of steam that the volume of the liquid remained practically constant throughout the digestions.

A great many different forms of filters have been tried for filtering the fiber. The most satisfactory form is by reverse filtration, using linen as a filtering medium. (The official method directs to use either linen, asbestos or glass wool.) Any good grade of linen is satisfactory. The first form of this filter was made as follows: A circular piece of linen was fastened over the mouth of a glass funnel by means of a draw string around the edge. The stem of the funnel is connected with the suction apparatus and the linen immersed in the liquid and the liquid sucked up into a waste bottle. The fiber adhering to the linen is washed off with a jet of water.<sup>1</sup> This form of funnel was used for a while, but was found unsatisfactory and was discarded on account of the fact that the linen was not supported and consequently sucked back into the funnel, causing trouble in washing. It also required a considerable amount of time to prepare the lined filters and attach them to the funnel. To overcome this difficulty Mr. Harris (formerly of this laboratory) designed a funnel made of sheet copper, the mouth of which is closed by a perforated copper plate, which supports the linen. The linen filter is fastened over this by a copper band about 1 cm. in width which fits closely around the edge of the funnel. This keeps the linen stretched taut over the copper plate and makes it very easy to wash off any adhering fiber. By this arrangement the linen filters can be changed very rapidly. The funnel, as used at present in this laboratory, is made 7 cm. in diameter, or so as to just fit into the fiber beaker, thus giving as large a filtering surface as possible. When the fiber is finally washed free from

alkali it is transferred from the beaker to a crucible or porcelain dish and evaporated to dryness in the usual manner. The only objection to the funnel just described is that in transferring the fiber it requires a large volume of water, usually 120 to 150 cc., to wash the fiber from the filter and wash out the beaker. To overcome this the author has designed a small copper funnel 3.5 cm. in diameter, made very similar to the large one. This can be used for the entire filtration, but the work can be done faster if the acid washings and the first few washings of the alkali are done with the large copper funnel, then on the last washing of the alkali use the small funnel. As the liquid is sucked up the funnel is carefully moved around in the beaker and the greater portion of the fiber can be collected on the linen attached to the funnel and can then be washed into a small crucible with a very small amount of water. It requires only a small amount of water to wash out the fiber remaining in the beaker. It was found that by using this method the fiber could be transferred to a small crucible with from 25 to 40 cc. of water as compared to 120 to 150 cc. with the large funnel. Where a large number of determinations are to be made this is a great saving in time as well as in the amount of gas burned in evaporating the fiber to dryness.

A number of tests were made, using Gooch crucibles for both the entire filtration or for the alkali filtration. The nature of the material causes the filters to clog so readily that it requires too much time to filter in this way when a more rapid method is available. Very satisfactory results were, however, obtained when all the washings except the last washing of the alkali were done with the copper funnel and the fiber then washed into the gooch. With wheat products and similar materials this procedure is fairly rapid, but with cottonseed-meal and similar products the filters clog very readily and it requires a considerable amount of time to complete the filtration.

Tests were also made with the Monroe crucible, prepared according to the directions given by Snelling.<sup>1</sup> When the filtrations were divided as described for the Gooch crucible, the Monroe crucible gave very satisfactory results. The time of filtration is, of course, longer than with the copper funnel, but this will be more than compensated for by the time saved on the evaporations. Snelling suggests the use of a platinum wire gauze in the platinum felt to prevent cracking and curling of the felt when heated. This would probably be of considerable advantage in this class of work. After the fiber has been ignited and weighed the ash can be very easily removed with a camel's hair brush without injuring the platinum felt.

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<sup>1</sup> *J. Am. Chem. Soc.*, **31**, 4, 1909.

<sup>1</sup> This form of filter was first gotten up by J. M. Pickel of this division. See preceding paper, *THIS JOURNAL*.

## PLANT AND MACHINERY.

## RECOVERY AND PURIFICATION OF SOAP LYE GLYCERINE BY THE GARRIGUES PROCESS.

By G. A. MOORE

Received April 15, 1910.

Glycerine is so closely associated with the soap industry that no soap plant is complete without its department for saving the glycerine contained in the fats and oils used by the soap maker.

For a number of years chemists and engineers have been directing their energies toward improved processes and machinery for the recovery of glycerine from spent soap lye. Many patents have been granted and many processes developed, each having the common object of glycerine recovery. A gradual evolution can be traced, the plants in successful operation to-day being but combinations of the old principles with new ideas, resulting in greater efficiency of procedure and improved design of apparatus.

Metallic salts, such as sulfate of iron and aluminum, were used in the early stages of lye treatment for coagulating and purifying agents, as in the processes of L. M. Brochon, in 1882, and Jesse P. Battershall, in 1883, and later by Jos. Van Ruymbeke, in 1891. The Van Ruymbeke process for recovering the glycerine from the still foots was an important step taken in 1894. In 1904 Garrigues developed his process for eliminating volatile fatty acids previous to distillation.

Domeier and Hagemann, in 1890, first used the closed salt separator later applied to vacuum evaporators by Foster, in 1899. O. Laist, in 1883, applied the air condenser to glycerine stills, but the first use of vacuum had been made in 1882 in connection with the apparatus of F. Armandy. In 1891 Van Ruymbeke combined the use of high vacuum with heating the still by means of saturated steam and injecting saturated steam and in 1894 applied the injection of expanded and reheated steam to glycerine stills. In 1904 Garrigues utilized the heat of the glycerine vapor from the still for superheating the low pressure steam injected into the still.

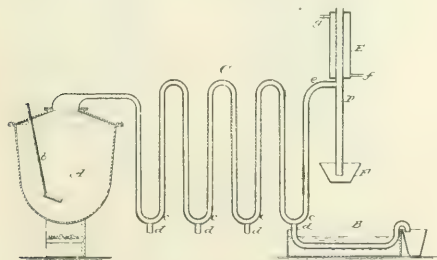


Fig. 1—Apparatus of O. Laist, 1883. Air condenser applied to glycerine still

With the Garrigues process the crude glycerine is of first quality, dynamite grade glycerine can always be produced in one distillation, and it is possible to obtain from even the blackest soap crudes a colorless, odorless, salt-free glycerine in two distillations, and there is never a time when the glycerine is off and has to be re-distilled.

Crude glycerine from soap lyes is a saturated solution of various alkaline salts in glycerine together with varying amounts of water, organic impurities and coloring matter. It is sold on a basis of 80 per cent. glycerine content and must contain but a small percentage of salts and organic matter in order to present but little difficulty in refining.

Refined glycerine must meet more stringent tests. Dyna-

mite grade must have a gravity at 60/60 F. of not less than 1.2602 and must contain not more than 0.01 per cent. chlorine as determined in the water solution of the ignited residue. Some

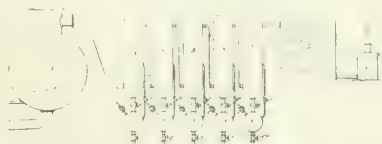


Fig. 2—Apparatus of F. Armandy, 1882. Vacuum still

buyers lay particular stress on the following silver nitrate test: Mix 10 cc. of glycerine with 10 cc. of 10 per cent. silver nitrate and stand in the dark 10 minutes. No precipitation or marked darkening in color must take place.

For chemically pure glycerine the tests as given in the United States Pharmacopoeia are official. C. P. glycerine must contain not less than 95 per cent. absolute glycerol, must be odorless and colorless, and conform to tests for mineral impurities, sugars, acids, salts, etc. Of the several tests designated in the Pharmacopoeia, that for butyric acid is most stringent and no glycerine will meet it. Also the silver nitrate test for acrolein is open to suspicion. In making this test the temperature must be taken into consideration, as any variation in temperature will invalidate the test. A good test is to mix equal volumes of glycerine and a 20 per cent. solution of silver nitrate and stand in the dark for thirty minutes. The solution should show no color in that time. The temperature must be kept constant by immersion in water at 15° C.

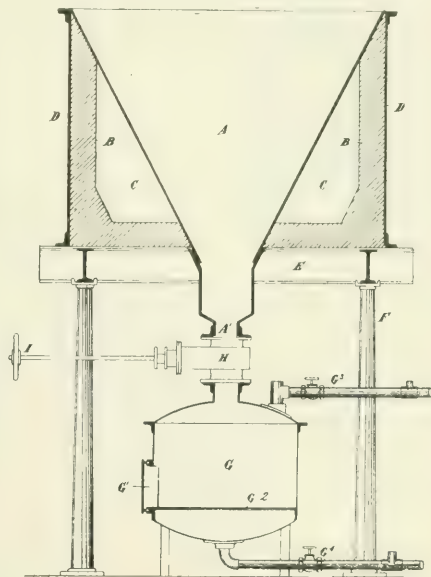


Fig. 3—Domeier and Hagemann's salt pan, 1890.

The presence of arsenic in glycerine used for medicinal purposes is extremely dangerous and pure glycerine should not show any reaction for arsenic by the following modification of the Gutzeit test. Place 2 cc. of sample in a high test-tube; add some zinc free from arsenic and a few cc. of pure dilute



sulfuric acid. The test tube is then covered with a tightly fitting cap of filter paper, two or three layers thick, the innermost layer having been previously moistened by the aid of a glass rod, with a 50 per cent. solution of silver nitrate. In presence of arsenic, arseniuretted hydrogen is given off. After ten minutes standing the paper cap is taken off and examined. No yellowish coloration should be noticeable. Distinction should be made in the sulfuric acid used in the process. That made from pyrites will almost always contain arsenic, while that made from brimstone does not.

Spent soap lyes as produced by the modern soap factory vary in quality, depending on the practice of the soap maker.

The refiner would, of course, prefer to receive lyes free from organic impurities and coloring matter, but the object of passing water through the kettle is to remove the dirt and coloring matter from the soap as well as to obtain a good yield of glycerine. It is advisable, however, to avoid running nigre and rosin lye to the glycerine plant. This, of course, can only be done if the glycerine has been properly removed from the soap before the nigre and rosin are added.

The yield of glycerine obtainable from the soap stock is entirely dependent on the amount of lye removed from the kettle. The best practice is to get about 90 per cent. of the glycerine in the stock into the crude. To obtain this yield necessitates the removal of at least three pounds of lye per pound of stock saponified, not counting the rosin used. The time to stop making

waiting to be treated and from which the separated soap can be skimmed. No lye need be drawn for the glycerine plant containing sufficient strength to raise the average of all the lyes to more than 0.4 per cent. total alkalinity. This low figure will result in a large saving both in caustic soda in the soap factory and acid used to neutralize the alkalinity of the lye in the glycerine plant.

After the lye has cooled and all separated soap been skimmed off, it is taken to the glycerine plant, where it is to be treated before going to the evaporators. The alkali in the lye must be neutralized and the organic impurities removed.

The neutralization of the alkali is effected by the addition of an acid, either hydrochloric or sulfuric. The use of the former is open to objection because of high cost. It has the advantage, however, of producing as a result of the chemical action, sodium chloride, and the salt recovered from the evaporator can be used continuously in the soap kettles. It also contains no arsenic—an advantage where C. P. glycerine is manufactured.

Sulfuric acid is most generally used. Its use introduces sodium sulfate into the lye, which salt is recovered with the common salt from the evaporator. Sodium sulfate is practically useless for graining soap, its graining qualities being but three-fifths that of sodium chloride and the grain produced is soft and often hard to separate from the lye. When the recovered salt has been used a sufficient number of times to bring the percentage content of sodium sulfate to 25 per cent. or 30 per cent., it is advisable to waste it, as with anything over this proportion so much is required to grain the soap that the large amount of salt is liable to give trouble in the evaporator by coating the tubes. The number of times recovered salt can be re-used depends on the amount of alkali left in the lyes.

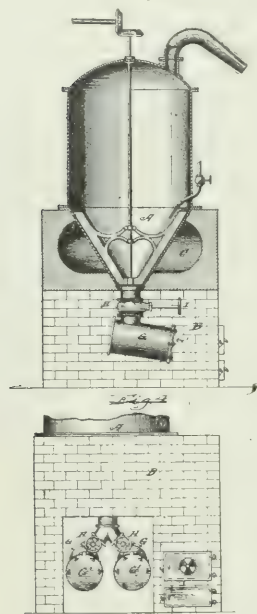


Fig. 4—D-meter and Hagemann's evaporator, 1890.

washes for the glycerine plant is when there can no longer be obtained a lye containing sufficient glycerine to pay for its recovery.

Spent soap lye as run from the kettle consists of water holding in solution the salt added to separate the soap, some soap (including lime soap), free alkali in the form of sodium hydrate and carbonate, aluminous matter in suspension as well as in solution, in certain cases gums, and the glycerine. If rosin and nigre lyes are used there will be much coloring matter from the rosin and nigre. All lyes will separate some soap on cooling and a storage tank should be provided for the lye

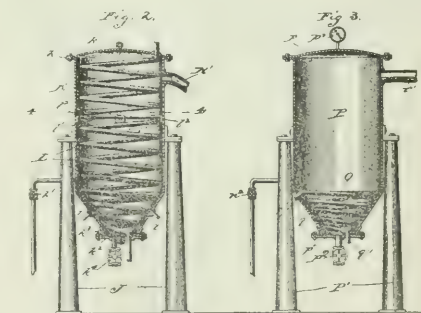


Fig. 6—Van Ruymbeke's still and concentrator, 1891

To remove the organic impurities some means must be employed to render them insoluble. This is best accomplished by the addition of metallic salts, forming insoluble metallic compounds, which are coagulated when the lye is brought to neutral. There are a number of compounds on the market for which special advantages in lye treatment are claimed.

For this work, however, the lower grades of aluminum sulfate are amply efficient and cheap enough to offset any advantage of the special chemicals.

The amount of aluminum sulfate to be used depends on the cleanliness of the lye and its freedom from soap and gelatinous matters. The least amount that will give a good cake in the filter press and not gum the cloths is the amount to use. This chemical can be added either dry or dissolved in water and will neutralize about one-third its weight of caustic soda. An excess of free caustic

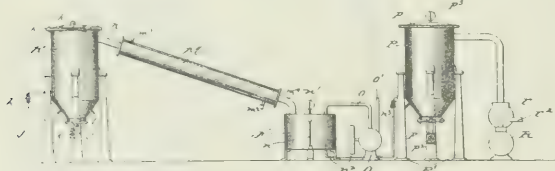


Fig. 5—Van Ruymbeke's still and concentrator, 1891

in the lye has a tendency to form aluminum hydrate which will retard filtering.

Some operators prefer to determine the amount of alkali in the lye by chemical analysis and then estimate the weight of acid to be added to bring the lye to neutral, making proper deduction for the amount of alkali neutralized by the aluminum

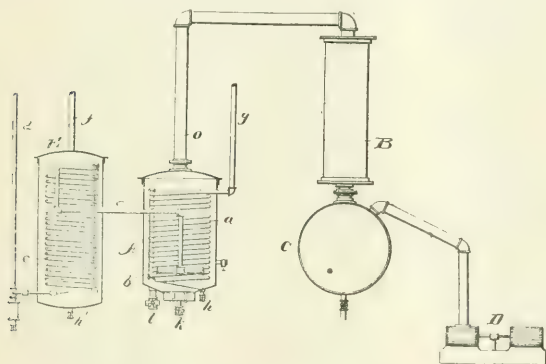


Fig. 7 Van Ruymbeke's still, 1894

sulfate. This, however, is unnecessary, as by means of a good neutral litmus paper in the hands of a careful worker the lye can be readily brought to between neutral and 0.01 per cent. alkaline (tested by the method given below, using phenolphthalein).

All lyes will contain some carbonate of soda. Carbonates in the lye have a tendency to cause foaming in the evaporator and as the action of carbonates on litmus is somewhat misleading the best procedure is as follows:

The lye is placed in the treating tank in which some means has been installed for agitating with air. With the air turned on, a portion of the acid is added—preferably just sufficient to take up the free caustic—then add the sulfate of aluminum. After the chemical is well mixed in, the lye should still be alkaline. Now enough acid should be added to just carry the lye

beyond the neutral point to the acid side, as indicated by its giving to neutral litmus paper a faint pink tinge. Care should be taken to thoroughly agitate the lye during all stages of the treatment.

If the lye were left in this acid condition there would be a tendency to re-convert some of the aluminum soap to aluminum sulfate and set the organic matter free, in which case both would go into solution in the acid liquor and pass through the press, producing a dark and gummy crude.

To avoid this state, the lye is made neutral or slightly alkaline by the addition of a strong solution of caustic soda. If the second addition of acid has been carefully made no more than one pint of 30° Bé. caustic need be added in treating 30,000 pounds of lye.

If the lye is just neutral it is well to make sure no chemical is still in solution. Filter a small sample and add a few drops strong ammonia. If there is any precipitate, add some more caustic to the lye and repeat the test. Usually the proper condition will be reached when the lye is between neutral and 0.01 per cent. alkaline. If desirable to know the exact condition of the lye, it is best determined by the following test: To about 20 grams of the filtered lye add 25 cc. distilled water and 5 cc. quarter-normal sulfuric acid. Boil for a few minutes to expel carbonic acid and titrate with quarter normal caustic soda, using phenolphthalein as indicator. If more acid is used the lye is alkaline. If more alkali it is acid. The difference between the acid and alkali used, multiplied by 0.01, divided by the weight of sample used and then by 100, is the per cent. alkalinity or acidity of the lye.

If the lyes being treated contain rosin lye or lye from the lower grades of grease, there may be an accumulation of a gummy material on the surface of the tank. This should be skimmed off, as it will gum the press cloths and make it hard to clean them, as well as retard the filtering of the lye.

The lye is now ready to be filtered and should pass through the press with little or no pressure. The press should drain into the tank from which the evaporator takes feed. With this treatment but one filtering is necessary, the filtered lye being practically water white. Lye containing an excess of alkali will have a yellow color and is often all but impossible to filter clear.

The practice of some soapmakers of returning silicated scrap to the kettles is to be condemned, unless all the lyes for the glycerine plant have been previously withdrawn from the kettle. This practice results in not only a loss in valuable filler but also a loss in acid neutralized by the sodium silicate in the lye treatment. The strongest objection, however, is that in treating the lye the addition of acid sets free silicic acid in its colloidal form, and any appreciable amount of this will retard filtering, and sometimes prevent the passage of any lye at even excessive pressures.

All lyes will contain nitrogenous matter, the amount varying with the care used in rendering. When the lyes are treated this is not removed, most of it appearing in the crude, increasing the figure for non-volatile organic residue. If the lyes are alkaline this nitrogenous matter partly decomposes in the evaporator, giving off ammonia. In the still this decomposition continues, the crude being always distilled alkaline, the ammonia passing out through the vacuum pump. There is no accumulation of nitrogen in the still foots when these are returned to the lyes, showing ultimate decomposition of all nitrogenous matter.

Crudes from cottonseed soap stock lyes contain nitrogenous acid bodies that resist this decomposition, necessitating waste

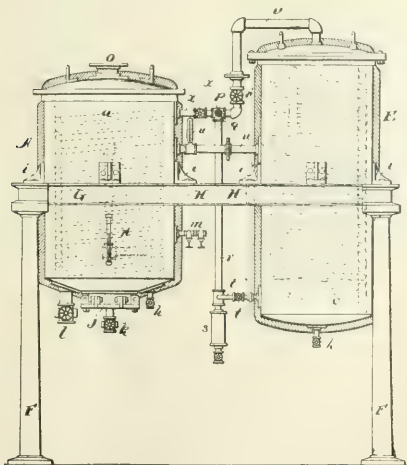


Fig. 8.—Details of Van Ruymbeke's superheater and still, 1894.

of the still residues. The same applying to crudes obtained by autoclave or Twitchell process from cottonseed soap stock black grease.

Lyes stored, free from caustic, ferment, the nitrogenous matter decomposing, producing sulfides which give off hydrogen sulfide on acidifying, and some glycerine is converted to trimethylene glycol.

fed, the tubes are thoroughly cleaned for the final concentration.

A finished crude can be obtained by double effect working, but there will be a big saving of time by working double effect to the half crude stage and then separating the double into two single effects and finishing the half crude, to crude using live steam at 15 pounds pressure.

In the Garrigues' evaporator the salt is separated and removed by the salt separator during concentration without interfering with the operation of the machine. It is thus possible to make finished crude in one operation, if desired, and still avoid trouble from the salt. This applies more particularly to the single effect machine, as finishing to crude in double effect is to be avoided, as stated above.

In his double effect apparatus, Garrigues has made the effects reversible by special arrangement of the vapor piping and valves. The advantage of this is quite evident. In double effect evaporation, when the desired concentration has been reached in the second effect and the machine is shut down, the first vessel will contain a liquor considerably heavier in gravity than the fresh lye. As the principle of successful double effect working demands a light liquid in the first effect, it is necessary to empty the first effect of this heavy liquor and start with fresh lye. Also the tubes of the second effect

would have a coating of salt, and if this partly concentrated lye, which might be at the salting point, was transferred to the second vessel it would not dissolve the salt from the tubes. The salt would then accumulate on the tubes and the machine would eventually have to be shut down for cleaning.

Now, if at the end of a run it is possible to reverse the effects, the machine is in ideal condition to start a new run. What was formerly the first effect containing a partly concentrated

Fermented lyes give considerable trouble in the evaporator by foaming. It is sometimes impossible to evaporate them. The sulfides also corrode the iron of the apparatus.

After filtration the lye is ready for the evaporator, and is to be concentrated to crude glycerine. This concentration may be accomplished in various types of evaporators, which may be operated either single or double effect. The use of evaporators of more than double effect is not practical in glycerine lye concentration, because of the difficulty encountered with the salt. In double effect work salt will often deposit in the first effect. If a triple effect machine were used, salt would always deposit in the second effect and because of the low vacuum under which the boiling in the second effect is accomplished, the tubes would become coated and interfere seriously with the proper operation of the machine.

If evaporators of the horizontal tube type are used or any type machine in which the salt from the entire run is accumulated and emptied after the machine is shut down, it is preferable to operate in two stages. That is to concentrate the lye to half crude containing from 30 per cent. to 40 per cent. of glycerol, and when sufficient of the half crude has accumulated to finish to crude containing 80 per cent. or more actual glycerol.

The large body of salt obtained when finished crude is produced in one operation is difficult to handle as the crude salt is harder to separate from the more viscous liquor. The large amount of salt obtained also gives trouble by salting the machine so that eventually it is found necessary to boil out with water to thoroughly clean the machine. Particularly is this so when sodium sulfate has accumulated to any extent.

By operating in two stages about 80 per cent. of the salt recovered is obtained from the half crude and the tubes at the end of a half crude run have only a slight coating of salt, which is effectually removed by the light lye when starting the next run. Then when finishing to crude, if the machine is filled with fresh lye and brought to a boil before any half crude is

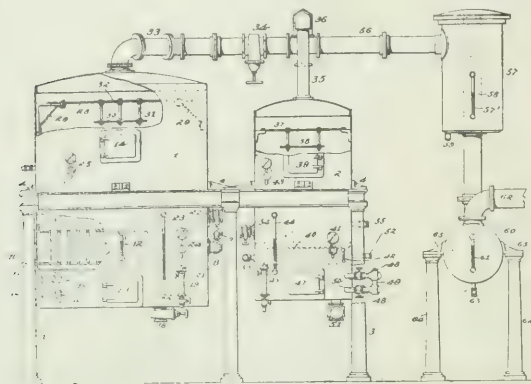


Fig. 9. Van Ruxmbeck's evaporator, 1894.

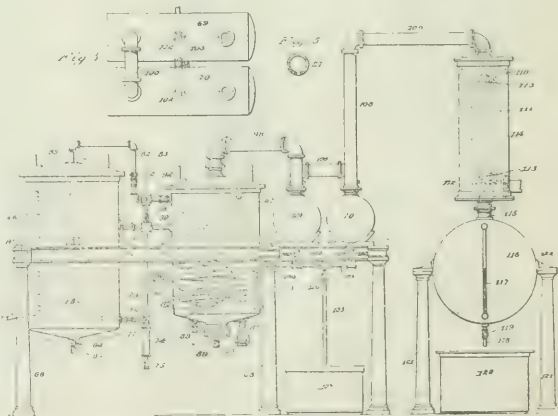


Fig. 10. Van Ruxmbeck's still set, 1894.

liquor and clean tubes has now become the second effect, and the second effect of the previous run with the tubes coated with salt has become the first. The tubes are then thoroughly cleaned by the fresh lye fed during the operation.

Crude glycerine contains varying amounts of organic matter, depending on the care used in the lye treatment, and alkali salts of the volatile fatty acids. The term "volatile fatty acids" is used among chemists to mean such fatty acids as vaporize



with water vapors at a temperature not exceeding  $212^{\circ}$  F. These include acetic, butyric, caprylic, etc., acids.

The presence of organic matter and alkaline salts materially retards distillation of the crude and increases the still residue. Furthermore, it is impossible to completely separate the gly-

cerine from the alkali salts of the volatile fatty acids, some of the fatty acids passing over to the distillate and some glycerine being retained in the still, the amount of glycerine retained increasing in proportion to the quantity of the alkaline salts in the still. In some instances the residues contain 50 per cent. of glycerine which cannot be readily distilled.

Garrigues has developed a process which by a sequence of various steps, concentrations, and addition of alkali largely eliminates the volatile fatty acids previous to distillation. There is thus in the still a very small amount of fatty acids as compared with the quantity of glycerine. As these volatile acids are partly distilled with the glycerine from even an alkaline liquid, it is apparent that the smaller the amount in the still the less will be the quantity found in the distilled glycerine. Also by almost entirely eliminating the volatile acids previous to distillation there is produced a residue so low in volatile fatty acid salts that the glycerine retained by them is trifling.

In this process the lyes, as received from the soap factory, are treated as has already been described. The insoluble aluminum soap is separated by filtration but the soluble fatty acids remain in solution as alkali salts and pass into the filtrate. After filtering, the lye is evaporated to half crude, containing 30 per cent. to 40 per cent. of glycerol.

The half crude liquor is separated from the salts crystallized during the evaporation. Sulfate of alumina is added in sufficient quantity to produce aluminum soap from all the insoluble fatty acids still present in the liquid in form of soluble alkali soaps. The liquid is now filtered and enough sulfuric acid then added to combine with the greater part or all of the alkali in combination with the volatile fatty acids. Thus the volatile fatty acids are set free. The liquid is again evaporated, the evaporation being continued until the liquid contains above 80 per cent. of glycerol. During this operation a further crystallization of salt takes place, and at

the same time the greater part of the volatile fatty acids is eliminated.

As the glycerine becomes more concentrated by the evaporation, a combination takes place between some glycerine and part of the remaining fatty acids producing glycerides, which

are identical with those contained in the original fat. Therefore it is not feasible to eliminate all the volatile fatty acids present during one evaporation.

The next step is to distil off the glycerine. At the high temperature necessary for doing this the glycerides of the volatile fatty acids contained in the liquid would again be decomposed by the steam into free fatty acids and glycerine. Both would distil and some glycerides would also distil unchanged. To avoid this contamination of the distillate a sufficient quantity of alkali is added to the still. This combines with the fatty acids present, holding the greater part of them in the still, probably in the original condition in which they existed in the lye. The liquid is now distilled. The operation is continued until nearly all the glycerine is distilled and only a small residue remains in the still. This consists essentially of sulfate and chloride of sodium, the alkaline salts of the fatty acids and some coloring matter, together with a small quantity of glycerine, and may be returned to the lye and again put through the process.

Theoretically considered, the elimination of volatile fatty acids may be brought about if in the first treatment the spent

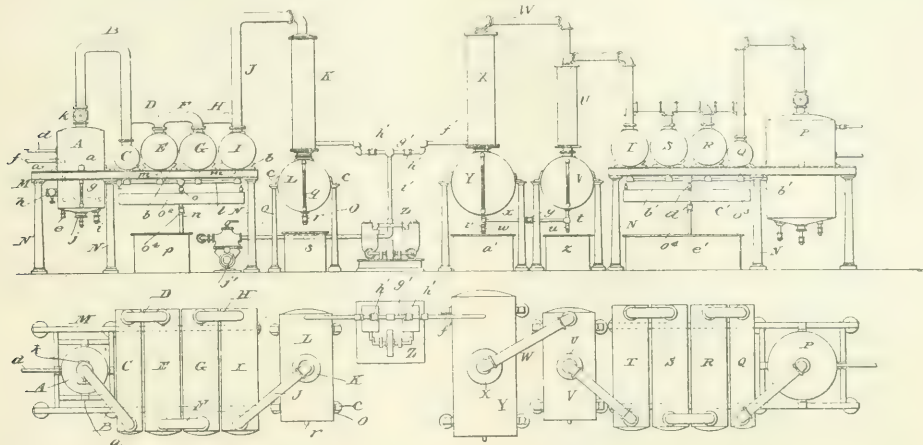


Fig. 11—Van Ruymbke's distilling plant, 1896.

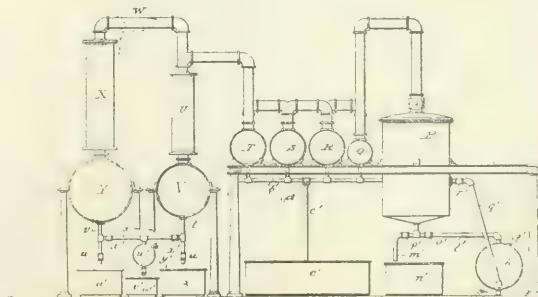


Fig. 12—Van Ruymbke's still set, 1896.

lye is made acid to such an extent that the volatile fatty acids are set free. These would then pass over with the water vapor during the subsequent evaporation of the lye. This plan is open to objection because the dilute liquid will froth violently during the evaporation if it contains free volatile fatty acids. This, however, does not take place if the acid condition of the

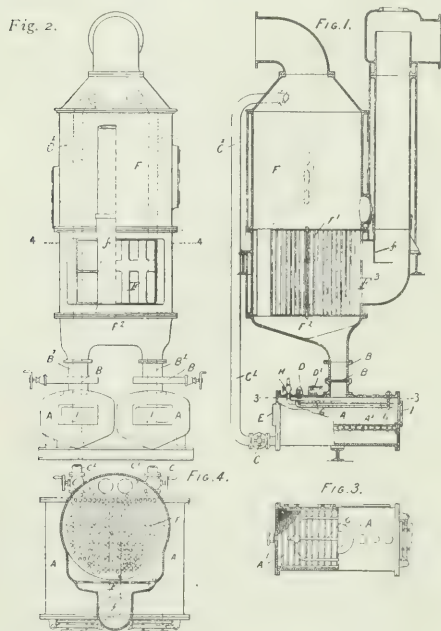


Fig. 13.—Foster's evaporator, 1899.

liquid is produced after partially concentrating the same, making it more viscid, due to a greater percentage of glycerine. Also the amount of dilute liquid to be handled would be so great that it would not be so easy to obtain the required conditions as when a small quantity of more concentrated liquor is treated. Waste lyes also contain some fatty acids which are sparingly soluble in water, but not readily volatile with water vapor. If the dilute liquor is acidified these acids pass into the filtrate because of the large amount of water present. If, however, a small quantity of concentrated liquid be acidified, these acids are largely precipitated and removed in the second filtration.

The machinery designed by Garrigues for performing the several operations of his recovery process is illustrated in the accompanying cuts.

Fig. 15 is a sectional detail of a vertical cast iron, steam drum evaporator. This evaporator is particularly adapted to the concentration of the acidified liquor. The acids volatilized during concentration have no material effect on cast iron, but will corrode steel plate. The evaporator consists of a cylindrical cast iron body with an internal steam drum arrangement for supplying the necessary heat for the evaporation. This heating arrangement is a cylindrical cast iron pot having a top cover sheet of rolled copper. Copper tubes pass through the pot and are expanded into the cast iron bottom and top copper sheet, making absolutely tight joints. The difference in expansion between the copper tubes and cast iron is amply provided for by the use

of the copper tube sheet and the construction of the iron pot as shown, thus avoiding leaky tubes. Steam is admitted into the drum by a pipe through the top of the evaporator and surrounds the tubes. This pipe is sufficiently large to allow the use of exhaust steam and is fitted with a curved conical dash plate above the drum. The condensation is carried away by suitable piping connecting into the bottom of the drum. The body is connected at the bottom to a salt extractor by a specially designed gate valve. This extractor is also cast iron and is fitted with sight glasses, vacuum gauge, and a salt odor for removing the salt. The bottom of the extractor is provided with a screen of brass wire cloth between perforated iron plates for draining the liquor from the salt. A vacuum break and steam connection are provided in the top. A suitable arrangement of piping connects the bottom of the salt extractor with the top and bottom of the evaporator and provides means for feeding and drawing off the liquor, breaking the vacuum in the machine, etc. The vapor is carried away by piping connecting into a cast iron catchall for retaining any liquor carried over by entrainment. The catchall in turn connects with some suitable apparatus for condensing the vapors and maintaining vacuum in the evaporator.

Fig. 16 is a steam drum evaporator of same principle as the cast iron evaporator. It is built entirely of steel plate and is provided with additional dash plates. Charcoal iron boiler tubes are used so no provision for difference in expansion need be made.

Fig. 17 is a double effect steel plate evaporator having the vapor pipes so arranged as to make the effects reversible.

Fig. 18 is a complete plant for producing crude glycerine, showing the several tanks with the filter press for treating and filtering the liquors, a Koerting exhaustor for agitating the liquor, and the evaporator with the salt extractor, condenser and vacuum pump.

Fig. 19 shows a complete distilling set arranged to illustrate the principle. The still into which the crude glycerine is fed is heated by means of high pressure steam in the closed coil, the temperature in the still being maintained at above 300° F. A pipe into the bottom of the still connects with a perforated cross through which superheated steam is injected into the liquid. The vapors pass off at the top through a pipe into a catchall for retaining any entrained liquors. The catchall is provided with a steam coil for keeping the vapors hot and preventing condensation at this point. From the catchall the vapors pass to the superheater, surrounding the tubes. A large part of the glycerine is here condensed and passes with the remaining vapors into the pipe leading to the cooler. The cooler is operated with hot water and the temperature of the water regulated by means of the cooling tank so as to condense nearly all the remaining glycerine in the vapors with but a small amount of the steam. The condensed liquor drops down and drains with that from the superheater into the concentrator. The vapors which pass the cooler contain a small amount of glycerine and are all condensed in the surface condenser and collected in the receiver below. A connection is made from

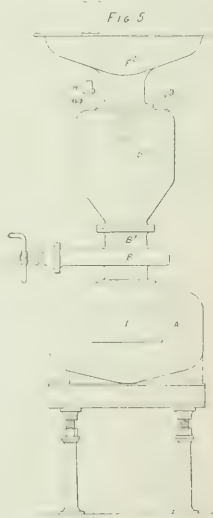


Fig. 14.—Foster's salt pan, 1899.

this receiver to a vacuum pump for maintaining vacuum in the entire apparatus. The liquor condensed in the superheater and cooler collects in the concentrator and is finished to gravity by high pressure steam in the closed steam coil, the water vapors driven off passing to the condenser with the vapors from the cooler. The liquor collected in the receiver, called sweetwater, is fed to the evaporator as produced. The evaporator is heated by means of a coil which receives steam from the outlets of the high pressure steam coils in the still and concentrator. The vapor generated in the evaporator being produced under reduced pressure because of the vacuum maintained in the apparatus has a temperature well under  $212^{\circ}$  F. This vapor

filter press by means of the pump, draining into the feed tank. When the entire charge is filtered the press is steamed out till live steam blows free from all the cocks, the liquor steamed out draining to the treating tank. After steaming, the press is opened and cleaned. The cake should be hard and dry and easily removed by wooden scrapers, leaving the cloths clean.

To start the evaporator the vacuum pump is started and then some water turned on to the condenser. The feed valve is opened and when the pump has raised sufficient vacuum the machine will fill. While the machine is filling the pump will be raising the vacuum and by the time the liquor has reached

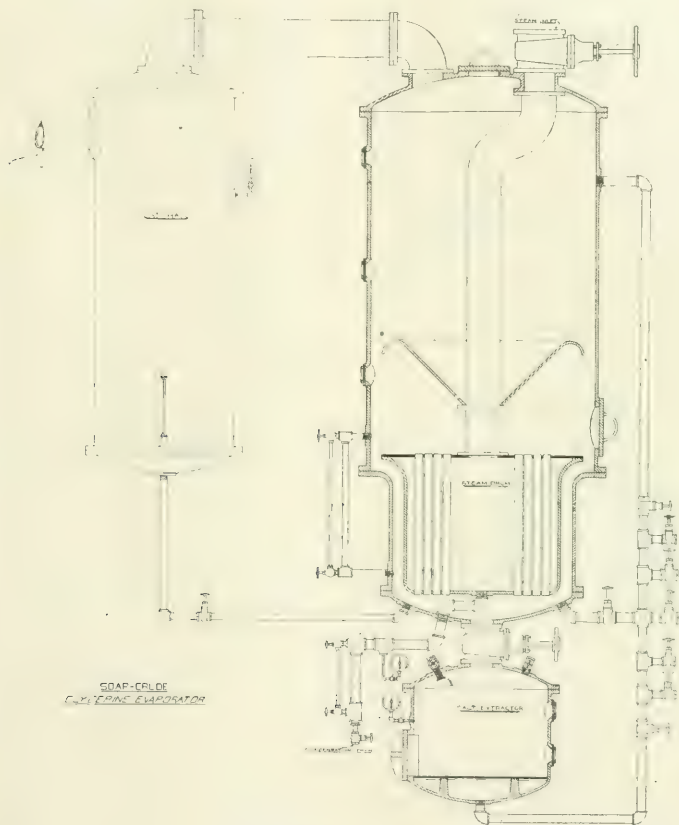


Fig. 15.—Garrigue's cast-iron evaporator

passes to the superheater and through the tubes. Here it is superheated by the hot vapors from the still which surround the tubes. The superheated steam then passes to the still and is injected into the liquor through the perforated cross, causing the glycerine to distil.

In describing the complete operation, reference is made to the complete crude plant, Fig. 18, and the still set, Fig. 19. The lye from the soap factory, with which the still residue from a previous run may have been mixed, is placed in the treating tank and treated with sulfuric acid and aluminum sulfate as already described; agitation being produced by means of the Koerting exhauster. The liquor is then passed through the

proper level, preferably about the top of the tubes, the vacuum will be about 25". The feed valve is closed and steam turned on, letting the liquor come to a boil slowly. The vacuum will fall at first and then recover quickly. Now more injection water will be needed and the full amount is turned on to the condenser. If the evaporator is given all the steam it will take without raising the pressure at the start to more than two pounds, the evaporation will be quite rapid. The feed valve is again opened and so regulated as to maintain a constant level in the machine.

As the evaporation continues, salt will begin to crystallize out and settle down into the salt separator through the gate



valve, which is open from the start. When the separator is filled with salt, as can be seen through the sight glass, the gate valve is closed. The connection from the bottom of the salt separator is then opened and the liquor drawn from the salt into the evaporator. This is accomplished by introducing an atmosphere of steam into the separator at the top, the vacuum then drawing the liquor into the machine by difference of pressure. After the liquor is all drained off the salt the atmosphere

tor. Then the gate valve is opened slowly and the liquor allowed to run into the separator, the feed valve being opened wide to maintain the level. This operation is repeated as often as the separator fills with salt. When the entire charge is fed to the machine, which will be near the end of the day, it is allowed to boil down to half crude of about 28° to 30° Bé. The evaporation is then stopped by first closing off the steam, then stopping the water to the condenser and shutting down the pump. The liquor is drawn off and pumped to the receiving tank.

When a sufficient amount of half crude has accumulated it is to be treated for eliminating the volatile fatty acids and finished to crude. The half crude is thoroughly agitated by the Koerting exhaustor (the connection is not shown in the cut) to insure its being uniform. If the half crude is alkaline it is first to be neutralized with sulfuric acid. To determine the quantity, 10 grams of the liquor are diluted with distilled water and heated to boiling. Phenolphthalein indicator is added and the liquid titrated with quarter-normal sulfuric acid, keeping the solution boiling hot. Each cc. acid used is equivalent to 0.10 per cent. caustic soda in the half crude, which requires 1.4 times its weight of 66° sulfuric acid to neutralize. This acid is added to the treating tank with the air turned on. If the half crude is not alkaline to phenolphthalein this operation is omitted. In either case the procedure is as follows:

A sample of the neutral liquid, 10 cc., is measured into each of say four beakers, and to them is added a 12 per cent. filtered solution of sulfate of aluminum, 120 grams per liter—about 1.5 cc. to the first beaker, and increasing by 0.5 cc. in each successive beaker. Filter in each case, and to the filtrate add more of the sulfate of aluminum solution. The test which remains clear on this second addition and contains the smallest amount of sulfate of aluminum, is the one to be accepted. If all remain clear, of course, too much was used in each case, and the test is repeated on a lower range, whereas if all becomes turbid, not enough was added in any case, and the test is repeated on a higher range. Usually the results are fairly uniform, so that a little experience with the process will determine the range to employ.

Each cc. of the aluminum sulfate solution used calls for 1 per cent. aluminum sulfate to be added to the liquid in the treating tank, and the required quantity should be dissolved in water by the aid of steam, and mixed into the charge, which is then to be filtered, the liquor draining into the feed tank. As this liquid is so rich in glycerine, the filter press should have an attachment for feeding hot water, so that the press cake may be washed, the washings going to the treating tank.

A sample of the clear filtrate, of about 2 grams, is evaporated free from water in a platinum dish covered with a platinum foil, and, when dry, it is completely incinerated. The dish is to be heated to a high temperature with a good gas flame; after cooling, the residue in the dish is dissolved in warm water and washed into a flask. Phenolphthalein and excess of quarter-normal acid are added. The solution is then boiled for a few minutes and titrated with quarter-normal alkali; making the test exactly as described for the spent lye, and also making the calculation the same way.

For each per cent. alkali, calculated as caustic soda present, add 1 per cent. 66° sulfuric acid, which will produce no separation in the liquid, if the previous treatment with aluminum sulfate was properly done. The liquor is now evaporated to crude glycerine, operating exactly the same as in making half crude except that steam at 15 pounds pressure is used, during which evaporation the soluble acids are expelled with the vapor. There must never be free sulfuric acid present, as this would corrode the evaporator.

All the soluble acid set free is not volatilized. As already

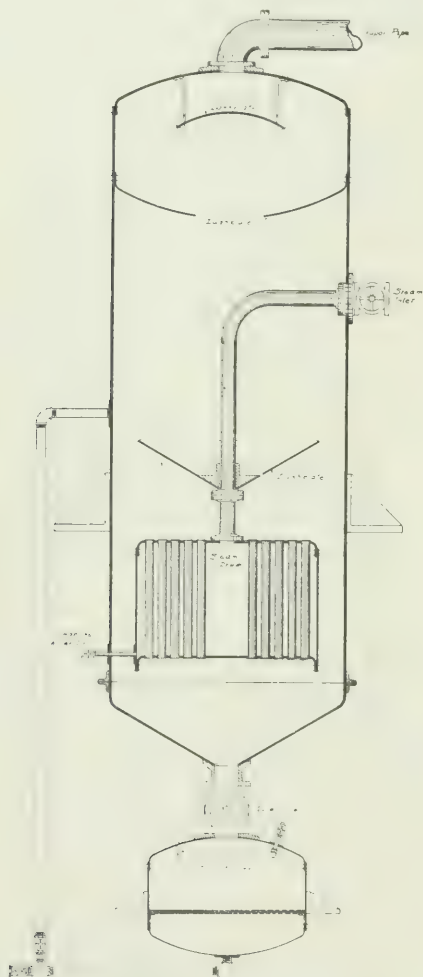


Fig. 16.—Garrigues' steel plate evaporator.

of steam is maintained in the separator for ten or fifteen minutes until the salt is thoroughly washed free of glycerine and dried. The steam is then turned off, the connection to the evaporator closed, and the salt removed through the salt door. The salt should be ready to be returned to the soap factory. Now the separator is closed and the connection to the top of the evaporator opened slowly to exhaust the air from the separa-

explained, when a certain concentration is reached, the free fatty acids combine with glycerine to form esters, and these are not volatile. In practice about two-thirds of the soluble acid

distillate. As the esters are saponified by the alkali to be added to the crude, as soon as boiling in the still begins, it is not sufficient that free alkali is present in the crude, but that

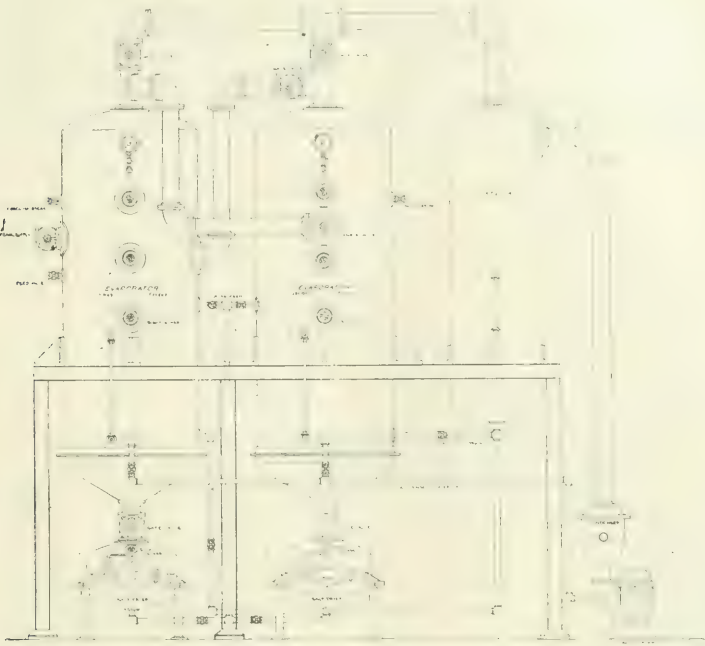


Fig. 17.—Garrigues' reversible double effect evaporator.

liberated by the sulfuric acid is eliminated with the water vapors.

The crude glycerine fed to the still must be alkaline, otherwise it may prime out of the still, and will also give an impure

enough be present to saponify the esters and still leave the liquid alkaline—about 0.3 per cent. of this excess alkalinity being the best amount.

To arrive at the quantity of alkali necessary to add to the

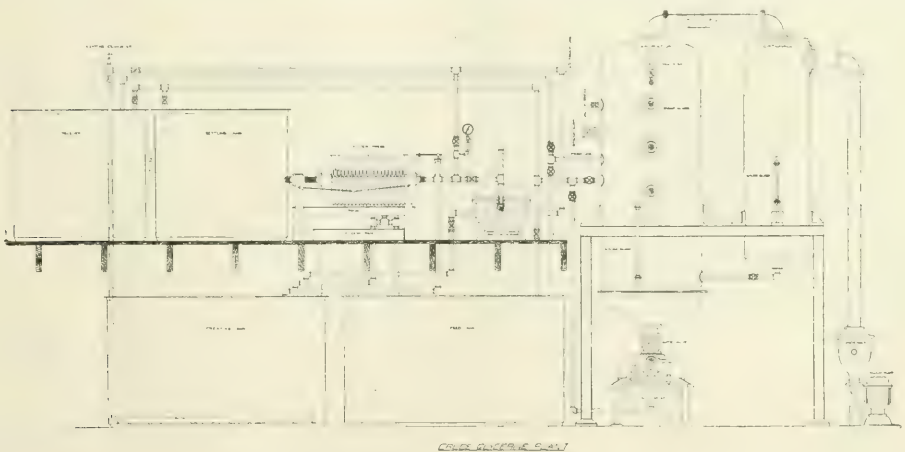


Fig. 18.—Garrigues' complete soap lye, crude glycerine plant.

crude, the esters must be saponified in making the test, which is done by boiling two grams of the crude glycerine, diluted with 100 cc. distilled water, with ten cc. quarter-normal caustic soda, for about fifteen minutes, and then adding phenolphthalein and titrating with quarter-normal acid, and the difference between the cubic centimeters acid and alkali used, divided by 2, is the per cent. caustic soda required to just neutralize the acid in the crude. This amount is added, plus the 0.3 per cent. free alkali desired to have present. The addition is best made in the form of a strong solution of caustic soda, obtaining the alkali strength from the specific gravity, by refer-

hot vapor from the still superheats the vapor from the evaporator so that it is delivered into the still at a temperature of about 300° F. (having received about 160° F. of superheat) and at a vacuum of 22" to 24". This abstraction of heat from the vapors condenses the glycerine in the superheater.

When the glycerin begins to distil a little water is started through the tubes of the cooler, regulating it so as to maintain a temperature of 140° to 160° F. in the overflow pipe. It is not desirable that all the glycerine be condensed here, otherwise all the volatile acids not eliminated from the crude will also condense and the crude will have too high an acidity. In

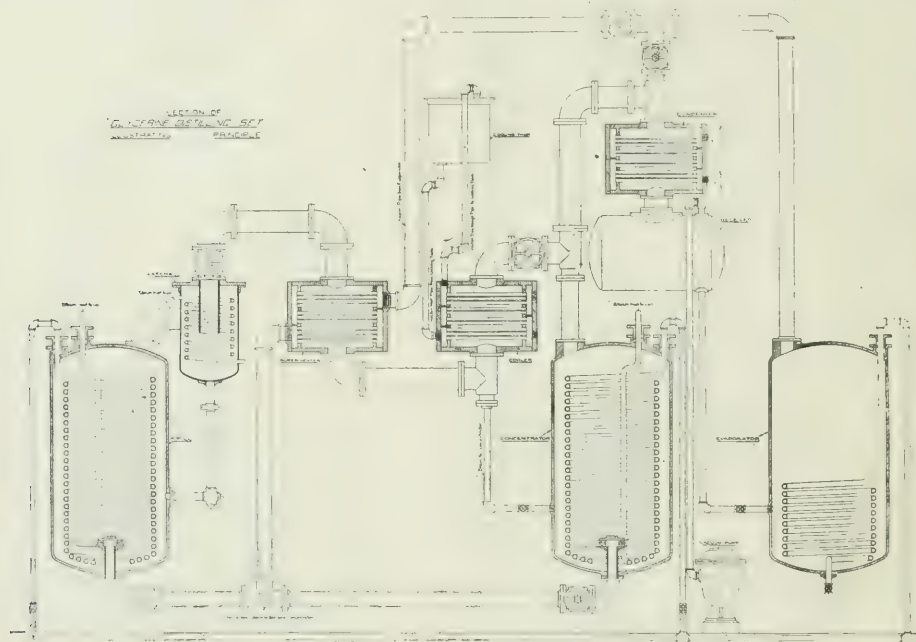


Fig. 19.—Garrigues' complete distilling set.

ence to an alkali table. The crude is allowed to settle free of salt and is then transferred to the still feed tanks.

To start the still, the vacuum pump is started first, having the valve on the pipe to the perforated cross in the still open. Then the sweetwater evaporator is filled to the proper level, with fresh water or sweetwater from a previous run. Also crude is fed to the proper level in the still. High pressure steam is turned into the still coil gradually, having the coil exhaust open to the sewer, till the still becomes hot. Then coil exhaust to sewer is closed and connection to the sweetwater evaporator coil opened, having exhaust of evaporator coil open to sewer. These conditions are continued till the sweetwater begins to boil. Then steam to the evaporator coil (from the still coil exhaust) is adjusted so that vacuum in the evaporator is between 22" and 24", the steam feed to the still coil having previously been opened wide. By this time the vacuum on the still will have reached a maximum, the higher the better.

Steam pressure of 140 lbs. is carried in the still coil, and the temperature of the vapors in the still is maintained at above 300° F., the corresponding temperature of the charge likewise being maintained by that part of the coil immersed in it. The

practice the cooler is so operated that the sweetwater will contain from 3 per cent. to 5 per cent. of the total glycerine which has to be redistilled because of the high acid content.

When these permanent conditions are established, the still and sweetwater evaporator are fed up to the level at which they are to be operated, and the feeding continued as required to maintain constant levels. As the distillation continues the concentrator will fill with glycerine. When this is about half full a little steam is turned on to the coil, just sufficient to evaporate the water condensed in the superheater and cooler. The coil exhaust is opened to the evaporator coil. Feeding the still is continued until the concentrator is nearly full and then stopped and the still allowed to run down. During this stage the vacuum may fall in the evaporator, due to the cross in the still clogging with foots. The steam-feed valve should not be changed, but if pressure appears, check the exhaust to save steam.

The still is shut down by first closing the steam valve to still and concentrator coils and opening the exhausts to sewer. Steam to the evaporator coil is then closed and also the valve on the injection pipe to still. The vacuum brake is opened and the



pump stopped. As soon as the vacuum is broken, the still drain should be opened and the residue allowed to drain into the foots tank, in which there should always be a few inches of liquid, and this should be mixed with the foots to keep them from hardening. The still should be washed out with hot sweetwater. The hot sweetwater is first pumped into a perforated pipe in the top of the still having the drain valve open. The drain is closed later and the still filled with sweetwater which is boiled with open steam. This operation to be repeated till still is clean.

If chemically pure glycerine is to be made, the first distillate should have a gravity of about 29° Bé. at 60° F. When the still is shut down, if sufficient steam has been on the coil in the concentrator, the distillate will be sufficiently heavy and need not be concentrated more. If, however, dynamite grade is to be made, the distillate is to be concentrated to gravity while the still is being washed. This is accomplished by closing the valve on the vapor pipe next to the cooler before breaking the vacuum, thus separating the concentrator and condenser from the rest of the set, the small connections from the vapor line below the cooler having also been closed. Operation of the pump and condenser is continued, having full steam turned on to the concentrator coil and the exhaust open to the sewer. When the desired gravity is reached, as shown by testing a sample removed by means of a sample tube (not shown), the steam is shut off, the pump stopped, the vacuum broken, and the distillate pumped to the dynamite bleaching tank. Here it is mixed with beaching carbon (about  $\frac{1}{4}$  to  $\frac{1}{2}$  pound per 1000 pounds glycerine—the amount depending on the color desired), then filtered and put into drums.

Crudes made from fermented lyes or lyes from fats that have not been washed before going to the soap kettle will always contain more or less trimethylene glycol. The gravity of chemically pure trimethylene glycol is only 1.05 and if present in sufficient quantity it is impossible to obtain gravity in making dynamite glycerine. In this case steam is injected into the concentrator the same as into the still and the glycol distilled off.

In making chemically pure glycerine, the first distillate is bleached with carbon the same as in the case of dynamite grade and redistilled. If the same still is to be used for the second distillation, it is necessary to remove all trace of the foots in washing the still. The best practice is to have a second still for this redistillation.

The operation for the chemically pure distillation is exactly the same as in the case of dynamite grade except that the sweetwater evaporator is always started with fresh water to avoid the odor of sweetwater from the crude. Not so much steam is required, however, in this operation and the sweetwater evaporator is operated so as to maintain vacuum in the evaporator from one to two inches less than at the pump. The slower the distillation is, the purer will be the distillate. Steam is turned on to the concentrator coil so that the distillate at the end of the run will have a gravity of about 1.253, at which it will contain at least 95 per cent. absolute glycerol. This distillate is pumped to the bleaching tank and mixed with bleaching carbon by means of air. About five pounds of carbon per 1000 lbs. of glycerine are added. It is then filtered and drummed.

Here again the presence of trimethylene glycol will cause trouble. While not objectionable in pure glycerine on account of gravity, it gives the product an acrid taste, which cannot be gotten rid of, as it is a property of the glycol. When redistilling to avoid bad effect of glycol, the first 10 per cent. distilled should be taken off and kept separate. In this manner any butyric acid present is also gotten rid of. The first 10 per cent. can be mixed with the crude and again be distilled, but unless dynamite grade is produced and some glycol gotten rid of that

way, the first 10 per cent. of the second distillation would eventually become chemically pure glycol.

## NOTES AND CORRESPONDENCE.

### DETERMINATION OF SULPHUR IN BRASS AND BRONZE.

For the determination of sulphur in brass and bronze, the method heretofore used has been rather circuitous by oxidizing the borings, filings or sawings with aqua regia, or with a solution of chlorine or bromine, repeated evaporation with HCl to remove the nitric acid or the other oxidizing agents, digesting with sodium carbonate filtering from the rather voluminous precipitate, and determining the sulphur in the filtrate by precipitation with barium chloride in the ordinary manner after proper acidulation.

The writer has attempted to adapt the method used for years for the determination of sulphur in organic compounds to the making of sulphur determinations in brasses and bronzes, and has been able to obtain thoroughly satisfactory results in the following manner.

With the aid of a mill-cut file, fine enough to make filings which will easily pass through a 100-mesh sieve, filings of the metal are prepared (file across machined face of test bar) and passed through a sieve. Any small particles of iron from the file are removed with the aid of a magnet.

One gram of these filings is thoroughly mixed with 6 grams of a powder consisting of 2 parts of potassium chlorate and one part of sodium carbonate.

In a wrought iron crucible there is first placed a small quantity of sodium carbonate to cover the bottom, then the mixture of the filings with the carbonate and chlorate is carefully transferred into this crucible, and finally the whole mixture is again covered over with a small quantity of sodium carbonate and chlorate. The crucible is then covered with a porcelain cover, and heated first slowly and then to a fairly high temperature over a Bunsen flame until the whole mass is thoroughly melted.

The fusion after cooling is digested with hot water. The salts which contain all the sulphur as sulphate, are filtered from the oxide residue, the filtrate is acidulated with hydrochloric acid and boiled to remove all carbonic acid. The solution is then neutralized with ammonia and made slightly acid by carefully adding hydrochloric acid until an acid reaction appears, and then 2 or 3 drops in excess are added. The solution is then brought to boiling, and a boiling solution of barium chloride is added.

Letting the solution stand for one-half hour in a warm place, but not boiling it further, all the sulphur will be precipitated as barium sulphate, which can then be readily filtered and washed.

The weight of the barium sulphate times 0.13734 is equivalent to the weight of sulphur in the sample.

Using an iron crucible does not appreciably increase the figures obtained, as the sulphur taken up from the iron amounts, at the outside, to  $\frac{1}{100}$  to  $\frac{2}{100}$  of 1 per cent.

If great accuracy, however, is required, a silver crucible can be used, or a nickel crucible.

It is self understood of course, that all the reagents must be tested for a possible presence of sulphur before they are used in this method.

GUSTAV THURNAUER.

LABORATORY OF THE  
LABORATORY METAL CO.,  
AURORA, ILL.

### THE WATER OF THE COLUMBIA AND WILLAMETTE RIVERS.

In the course of some soil investigations which are being carried out at this Station we have had occasion to collect

for analysis monthly samples throughout the year from the Columbia and Willamette rivers. As the composition of these waters has not been recorded so far as known by us, the following analyses made by Mr. B. Pilkington of this department may be of interest.

The Willamette sample was collected at Corvallis July 18, 1909; the Columbia water was taken August 6, 1909, at Mayer, Oregon, a point about fifty miles above the river's mouth. The Willamette at the time of sampling stood 1.7 feet, and the Columbia 9.1 feet above low water.

	Columbia.		Willamette.	
	Parts per million.	Per cent. of total solids.	Parts per million.	Per cent. of total solids.
CO <sub>2</sub> .....	16.4	31.66	1.1	3.08
SO <sub>4</sub> .....	5.5	10.62	4.7	13.13
Cl.....	5.5	10.62	4.4	12.29
PO <sub>4</sub> .....	0.08	0.15	0.08	0.22
Ca.....	8.7	16.80	3.8	10.61
Mg.....	2.5	4.83	1.0	2.79
Na.....	4.0	7.72	4.9	13.69
K.....	4.1	7.91	2.8	7.82
NH <sub>4</sub> .....	0.42	0.81	0.52	1.45
Si.....	2.4	4.63	12.1	33.80
Al <sub>2</sub> O <sub>3</sub> .....				
Fe <sub>2</sub> O <sub>3</sub> .....	2.2	4.25	0.4	1.12
Total.....	51.8	100.00	35.8	100.00

The Columbia water is seen to be relatively rich in carbonate of lime obtained no doubt from its upper course where lime formations are found. The soil of the Willamette Valley, on the other hand, contains only traces of carbonates, which is reflected in the low content of carbonates in the Willamette water. The tributaries of the Willamette are generally high in silica. The ammonium in the samples was calculated from the value for total nitrogen.

C. E. BRADLEY.

AGRICULTURAL EXPERIMENT STATION,  
CORVALLIS, OREGON.

## BOOK REVIEWS AND NOTICES.

Reports of the Chemical Laboratory of the American Medical Association. Vol. 1. From its establishment to Jan. 1, 1909. Vol. 2, Jan. to Dec. 1909.

Reprint of the Reports of the Council on Pharmacy and Chemistry of the American Medical Association with the comments that appeared in THE JOURNAL during 1905-8, Vol. 1, and 1909, Vol. 2. Published by THE AMERICAN MEDICAL ASSOCIATION.

In no other country are there more drugs and medicines consumed per capita than this. Also nowhere else has the sale of patent medicines and proprietaries assumed such tremendous proportions, resulting largely from the extravagant claims. In order to protect the public as well as the medical practitioner from this avalanche of medicines, the American Medical Association appointed in 1906 a committee known as the Council of Medicine and Pharmacy, aided by its chemical laboratory of which Prof. Puckner is the director. The duty of this committee is to examine all remedies applying for recognition before the medical profession, rejecting such as make fraudulent claims as to origin, unwarranted or misleading therapeutic claims, secrecy as to composition, or objectionable advertising, etc.

The Reports of the Chemical Laboratory, serve to give in concise form, the various methods employed in the analysis of the preparations submitted. These afford much valuable information to the general analyst not obtainable elsewhere. The Reports of the Council represent the results of the scientific investigations including all clinical and pharmacologic data as well as comments. Among these, the reports on Medicinal

Foods, Diastase Ferments, Formaldehyd Derivatives (Vol. 1), Isopral and Bromural, show an immense amount of painstaking labor on the part of the chemist and pharmacologist. In this connection attention is called to the "New and Non-Official Remedies," a volume of 356 p. which gives descriptions and tests of all remedies recognized up to June 1, '10.

To give the reader an insight into the kind and variety of work accomplished, a few instances may be cited. An example of a misleading label is "Tyree's Antiseptic Powder" which states it to contain, borax, alum, phenol, glycerol, thymol, eucalyptol, gaultheria and mentha (?), was found to consist essentially of zinc sulfate and boric acid with traces of phenol. Thialion a "sodio-trilithic anhydrosulphate" of formula  $3Li_2O \cdot Na_2O \cdot SO_3 \cdot 7H_2O$  was found to consist of a mixture of sodium sulphate and citrate with small quantity of lithium citrate. The need of an invasion into the field of galenicals, is illustrated by the results of an examination of unofficial non-alcoholic fluid extracts of Hydrastis (Golden Seal). Preparations of this drug are extensively used, and the selling price varies between \$1.25 and \$4.50 per pound, although all are claimed to be of same strength. Assays demonstrated the yield to be between 0.58 and 1.79 grams of hydrastin per 100 cc., while the Pharmacopoeia standard demands 2 grams alkaloid per 100 cc. Worth careful study are the methods recommended for assay of Phenol, Hexamethylene Tetramine, Castor Oil in Powder form, Croton in Castor Oil, Mercury and Iodin in Mayer's Reagent, Pepsin and Bismuth Preparations, etc. (Lab. Reports).

We note the melting point of urotropin is given at 194.200°. On page 35, Vol. 2, Laboratory Reports, we note that the presence of bismuth sulphid is based on the conclusion that hydrogen sulphid is given off upon the addition of hydrochloric acid to a mixture containing bismuth sulphonate, zinc oxid, etc., the operator not having noted the presence of ultramarine blue added as color corrigent. Under Medicinal Foods (Peptonoids, Predigested Beefs, Panopeptone, etc.), none are approved that contain less nutritive value than milk, and at least 1/4 of the value shall reside in the nitrogenous matter. Such legitimate pharmaceuticals as Taka-Diastase, Maltzyme, Holadin, etc., come in for their share of criticism in that grossly exaggerated claims are made, further that "to be of value, statements regarding the digestive power of diastase should be based on standard and uniform methods of testing." The Council has adopted methods of its own against the vigorous protests of some of our largest manufacturers in this line. In adopting standard methods, it would be no more than just and reasonable, that manufacturers who have devoted their entire time to the study of such products be consulted and their methods given a fair trial. It is through such coöperation and study, that a uniformity of methods is secured in conjunction with the good will of firms whose integrity and experience is beyond question.

We must realize that errors of judgment and experiment are possible under all conditions, and where a policy of "control" is to be exercised by a body of analysts and clinicians, the greatest care should be exercised in formulating standards. Analysts may differ and clinicians usually differ, since therapeutics is not as yet an exact science. The judgment of those whose field lies within a special line should never be ignored.

Nothing is gained by a "hammer and tongs" policy (perhaps necessary in patent medicine line, when applied towards legitimate manufacturers, they are amenable to reason, but once antagonized, their united opposition may sometime overthrow all the good that has been and will be accomplished by the Council.

V. COBLENTZ

Fungus Diseases of Plants. By BENJAMIN MINGE DUGGAR. Cloth. 8vo. XII + 508 pp. Ill. Boston, Ginn & Co. 1909.

This book is based principally upon the investigations of the

past thirty years on the fungus diseases of plants and it is the only work of American origin available to the student on the subject. In plan and execution the work is excellent. The contribution of chemists to the subject lies principally in the methods of disease control by the use of fungicides. It would appear that there is an immense field here for the investigator. At present the use of fungicides is based entirely upon empirical knowledge, and it is probably true that it is based largely upon information accidentally acquired. Systematic investigation on the many possible fungicides is but beginning. It goes without saying that the work will be found of value to mycologists and it would also prove of value to the chemist working in this field. The book is well bound, printed and illustrated and typographical errors are few.

The University, of Illinois, Engineering Experiment Station, has just issued three bulletins of great interest to students and users of fuel. *Bull.* 37, Unit Coal and the Composition of Coal Ash, by S. W. Parr and W. F. Wheeler; *Bull.* 38, The Weathering of Coal (series of 1909) S. W. Parr and W. F. Wheeler; *Bull.* 39, Tests of Washed Grades of Illinois Coal, by C. S. McGovney. The titles of these bulletins indicate the ground covered and the reputations of the authors will speak for the quality of the contents.

From the University of Wisconsin comes *Bull.* 346, on the subject of Alloys of Nickel and Copper with Electrolytic Iron, by Chas. F. Burgess and Jas. Ashton. This is a valuable contribution to the literature on binary alloys of iron with the common metals—a fruitful field for the student, which has not received as much attention as it deserves.

**Dust Preventives and Road Binders.** BY PREVOST HUBBARD, New York, Wiley & Sons, Octavo vi + 416 pps. illustr. \$3.00 net.

Although at first thought it would seem to one who has been connected with the construction of highways for many years that the present is hardly the time to write a book on the subject which Mr. Hubbard has selected, in view of the fact that it is still in a highly experimental and transitional state, the author has assembled in a very satisfactory way many data, some original with him and more taken from the publications of others, in regard to various materials employed at the present time as dust preventives and road binders and as to their preparation and use, all of which will prove of great value for reference to many engineers and public officials who are constructing and endeavoring to improve the character of our highways. He has also presented some of the conclusions bearing on the application of these materials, which have been arrived at in the Office of Public Roads of the United States Department of Agriculture during recent years which, although many of them available in the bulletins of that office, are justifiably republished for general use. Mr. Hubbard's chapter on "The Examination of Bituminous Road Materials and Interpretation of Results" will be acceptable to the numerous chemists who are taking up such work for the first time, as is now frequently the case, and will prove of interest to the more expert operators.

Where the author advances opinions as to the merits of various materials, he hardly seems justified in all his statements in view of the fact that service tests, from which the only satisfactory conclusions can be drawn, have not extended over a sufficiently long period to lead to anything definite. Undoubtedly many of the statements involving mere opinion, which the book contains, will necessarily require modification in the future, but as a whole the book has a present usefulness which commends it.

Mr. Hubbard has wisely avoided the use of trade names and

in most respects, has handled his subject impartially and with a scientific spirit. The style in which the book is written is excellent and it will undoubtedly have the large circulation which it deserves.

CLIFFORD RICHARDSON.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building 908 G St., N. W., Washington, D. C.

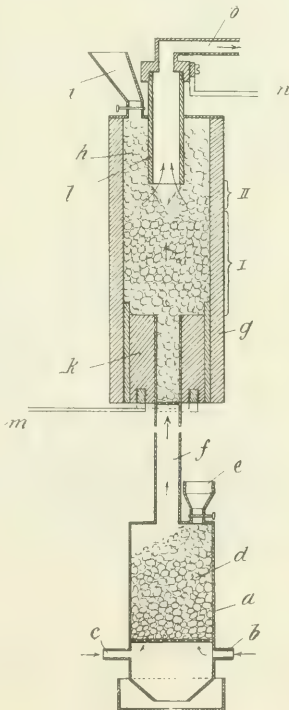
Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**954,080. Process of Producing Hydrocyanic Acid.** O. DIEFENBACH AND W. MOLDENHAUER, DREISLACH, Germany, April 5, 1910.

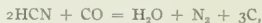
It is well known that hydrocyanic acid can be produced by passing a mixture of nitrogen and hydrogen over highly heated carbon, and recent experiments have, moreover, demonstrated that a proportional yield as high as 35 per cent. can be obtained at temperatures of about 3500° C.

For the industrial application of this process a cheap and simple method of producing the necessary nitrogen-hydrogen mixture is of importance. Since the production of pure nitrogen and hydrogen, by whatever method attained, involves considerable expense, the question arises whether the mixtures of the same with carbon monoxide or carbon dioxide, which can be cheaply and easily produced commercially, are suitable for the purpose in view. From the theoretical standpoint, it would appear that the possibility of so applying these mixtures





is very small, for since hydrocyanic acid at high temperatures is capable of reacting with carbon monoxide, according to the equation:



it might certainly be expected that it would not be formed at all in the presence of carbon monoxide or that it would be destroyed by the latter immediately upon its formation. When it is found that this view is contradicted by experiment, the only explanation possible is that the rapidity of the above reaction is not sufficiently great when, under suitable experimental conditions, the gas-mixture is subjected to rapid cooling, as to permit of the decomposition of large quantities of the hydrocyanic acid newly produced. If, for instance, the mixture known as Dowson gas, which consists chiefly of hydrogen, carbon monoxide, nitrogen and a little carbon dioxide, is led over carbon which—by any suitable means—is maintained at a very high temperature, more or less considerable quantities of hydrocyanic acid can be detected in the gases rapidly aspirated from the furnace, according to the degree of temperature at which the process is conducted.

The hydrocyanic acid thus produced can be employed for the production of other cyanogen compounds, or may be transformed into ammonium sulphate by passing it through concentrated sulphuric acid. The hydrogen and nitrogen which have not undergone transformation into hydrocyanic acid together with the carbon monoxide mixed therewith may, after the removal of the acid, be again passed over incandescent carbon for the purpose of obtaining a further yield of hydrocyanic acid, or they may be applied to heating purposes.

The accompanying illustration shows an apparatus used by the patentees in practicing their process.

954,827. Electric Induction Furnace. C. W. SODERBERG, Ski, near Christiania, Norway, April 12, 1910.

An electric induction furnace theoretically consists of a transformer with short circuit in its secondary coils, the latter mostly consists of one or more liquid metal baths, which replace the coils, the ohmic resistance of which is so adjusted, that a middle load is obtained. It is important, in order to obtain a minimum leakage of the power lines, that the disc transformers have the

In this furnace the primary windings are distributed on four coils as  $a^1$ ,  $a^2$  enclosing both of the vertical parts  $b^1$ ,  $b^2$  of the iron core. The secondary armature consists of a metal bath,  $m^1$ ,  $m^2$  contained in a hearth  $m$  arranged between the primary coils and formed with an intermediate portion, and two semi-annular channels  $e^1$ ,  $e^2$ , which together with the intermediate portion enclose both of the vertical pieces of the iron core. By arrangement of four coils the leakage of the power lines is cut down to about one-fourth of what it would otherwise have been under similar circumstances.

The lower primary coils are cooled by currents of air which pass through channels  $d^1$ ,  $d^2$  in the foundation of the furnace which may be of masonry or any suitable material as the effect of the intensity of the current is proportional to its square; the above-mentioned cooling diminishes the resistance and the intensity of current is increased. The efficiency of the furnace per unit of time thus increases, an advantage which is the more important in this construction, because the coils enclose both of the vertical legs of the transformers.

In order to facilitate the metallurgical operations, which are rendered difficult on account of the primary coil covering part of the metal bath, the extended parts of the baths are situated outside of the current carrying parts of the bath and not covered by primary coils. Such channels have been used in some prior constructions, but never in furnaces of the disc-transformer type for the above-mentioned purposes of providing working space, the metallurgical operations, the feed, and the treatment of the slag are facilitated and repairs may be easily made without removing any part of the primary coils of the furnace.

956,381. Process for Treating Ores. A. A. LOCKWOOD AND M. R. A. SAMUEL, London, England, April 26, 1910.

This invention relates to the treatment of such sulphide ores, tailings, middlings, or concentrates, as are difficult to separate into their constituents owing to their physical formation. This difficulty is usually caused by the pseudomorph formation of the ore; this is the case for example in complex lead and zinc ores such as Broken Hill ores.

According to this invention crushed ores, under which term it is intended to include tailings, middlings or concentrates, are subjected to a preliminary treatment of agitation with a reagent or reagents in such a manner that the incrustations are sufficiently attacked to free the metallic particles so that they can be classified by any known means. In some cases improved results may be obtained by first heating the ore or the like to a temperature preferably just below that of desulphurization. As reagents there are employed solutions of substances such as caustic alkali or sodium or potassium silicate which may be used either separately or in succession or in combination according to the ore to be treated. The quantity of the reagent and water necessary and the length of time required for the treatment will differ more or less according to the ore to be treated, it should be such that the incrustations are loosened while the metals remain undissolved.

As a comparative example of the treatment, a parcel of two tons of Broken Hill proprietary ore of a very complex formation was taken and crushed to about 40 mesh to the linear inch. 2,240 lbs. of this was treated with a solution containing about 5 per cent. of caustic soda and 1 per cent. of silicate of soda in the proportion of 25 lbs. of the solution to each 100 lbs. of ore. After agitating for about 30 minutes the pulp was fed onto sizing screens and thence passed to a vanning table. The result of this treatment was as follows, the scale of the mesh to the linear inch being 60 and 80—103 3/4 lbs. of coarse (plus 60) galena (dried), 172 lbs. of fine (plus 80 and minus 80) galena and 43 3/4 lbs. of zinc lead middlings from the coarse and 36 1/2 lbs. middlings from fine. The assay value of the galena was 76.8 per cent. lead with 3.9 per cent. zinc and the middlings

Fig.1.

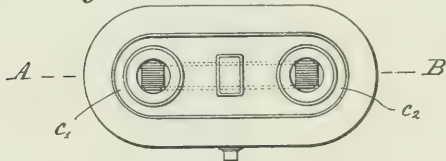
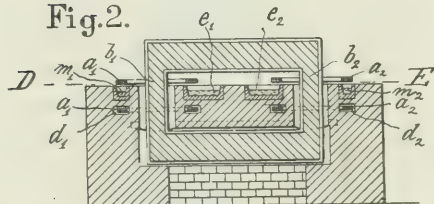


Fig.2.

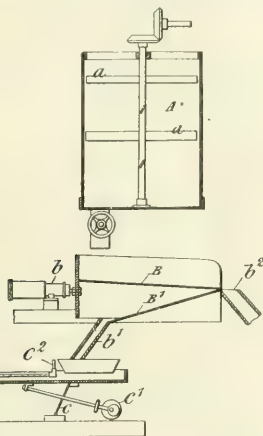


coils so distributed, that the whole number of ampere-turns is not concentrated to one coil.

The object of this invention is to provide an induction furnace of the disc-transformer type, in which this electrical feature as well as means for facilitating the metallurgical operations are embodied.

contained free galena and free blende. The remaining 2240 lbs. of the ore was treated in the same manner including the agitation for 30 minutes with water but without the addition of caustic or silicate. The result was 88 lbs. of coarse (plus 60) galena, 134 lbs. of fine (plus 80 and minus 80) galena and 130 lbs. of zinc lead middlings from the coarse and 68 lbs. middling from the fine. The assay value of the galena was 72 per cent. lead with 6.5 per cent. zinc, while the middlings appeared to be quite inseparable and further crushing would have been required to free the metallic particles from one another.

It is quite obvious that the treatment may be applied as in the example to the ore in bulk or the metallic particles may be concentrated by an oil or similar selective process and then treated and classified or of course the crushed ore may be taken and passed over the table before treatment getting as much



free galena as possible, then taking off the table for treatment a large line of middlings containing the incrustated particles. The middlings are then treated as before described and passed over a table or otherwise classified. The particular method of treatment to be adopted will easily be found by the aid of a few experiments, which will show whether it is more profitable to treat the whole first, or to treat the middlings or the concentrates or tailings, together or separately.

In dealing with ores for treatment, a few tests will be necessary to ascertain the degree of fineness to which they should be crushed before treatment and this will vary with the formation of the ore and may also be varied to suit the particular method of concentration to be employed, but speaking generally the ore should be left as coarsely crushed as possible and this for two reasons, viz.: in order to reduce the amount of slimes formed and because of the decreasing advantage of such a treatment, for it will be obvious that with a pulverized ore the incrustations will no longer be present and the more finely the ore is crushed the more the incrustations will be broken down and the less need there will be for the treatment except when overcoming or preventing the acquired tendency of particles to adhere together when the ore is treated with oils or the like.

The accompanying illustration shows the apparatus employed in practicing the process in this illustration.

In the drawing A is a vessel provided with an agitator *a*. B is a sizing screen, B' a second and finer screen inclined in opposite direction to the first. The combined screens are directly connected to the piston of a reciprocating engine *b*. *b'*, *b''* are delivery spouts.

The coarse and the finer ore is treated on a vanning table

at different times. As shown the finer ore is delivered onto a vanning table.

C is a vanning table supported on springs *c* and reciprocated by means of an eccentric *c'*.

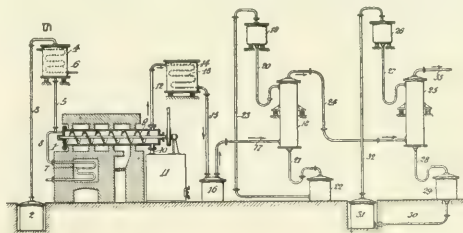
*c''* indicates means for supplying water to the table and *c'''* indicates a chute into which the heavier parts fall.

**956,184. Process for Obtaining Sulurous Acid from Acid Sludge.** G. SCHILDHAUS AND CONDREA, Capina, Roumania, April 26, 1910.

It has now been found that acid tar may be distilled with good results by introducing heated air into the retort during distillation and thereby oxidizing the sulphur and its compounds. In this manner three products are obtained from the tar: (1) A mixture of gases mainly consisting of sulphurous acid, nitrogen and air and containing small quantities of carbonic acid and gaseous hydrocarbons. (2) Liquid hydrocarbons. (3) Coke. The tar is preferably vaporized at a comparatively low temperature of between 250 and 350° C. and the air introduced into the retort is preferably heated to the same temperature. The acid tar is run into the retort in a thin stream. The coke remaining in the retort is porous and brittle and is continuously evacuated by a mechanical device and transported to a closed chamber. The gases that issue from the retort are conducted through a cooler to condense the liquid hydrocarbons, and are then washed first by means of heavy hydrocarbon oil and finally by means of concentrated sulfuric acid to remove the gaseous hydrocarbons and the last traces of the vapors of liquid hydrocarbons.

The illustration shows a diagrammatic side-view of the apparatus for carrying out the process.

The process is as follows: The tar is introduced in a thin stream into the retort 1 from the monteju 2 through the pipe 3, vessel 4 by means of the heating coil 6. In the retort 1 the tar is vaporized, preferably at a comparatively low temperature of between 250 and 350° C. The air is preferably heated to the same temperature by means of the heating coil 7 and is introduced into the retort 1 through pipe 8. The coke remaining in the retort is porous and brittle, and is continuously evacuated by the feeding screw 9 through the pipe 10 into the closed chamber 11. The gases issuing from the retort 1 are conducted through the pipe 12 and cooling coil 13 which lies



within the condenser 14. The larger part of the liquid hydrocarbons is condensed in the cooler and fed through pipe 15 into the vessel 16. The gases escaping from the vessel 16 are fed through pipe 17 into the scrubber 18 in which they are washed by means of heavy hydrocarbon oil which is run continuously from the vessel 19, through the pipe 20, through the scrubber 18 and the pipe 21 into the vessel 22 and back to the vessel 19, through the pipe 23. The washed gases escape from the scrubber 18 through the pipe 24 and enter the scrubber 25, where they are washed with sulphuric acid which is contained in the vessel 26 and flows through the pipe 27 into the scrubber 25, pipe 28 to vessel 29 and pipe 30 to the monteju 31 wherefrom it is fed back through the pipe 32 into the vessel 26. By washing the gases with heavy hydrocarbon in the scrubber 18

and afterward with sulphuric acid in the scrubber 25 they are freed from the last traces of the gaseous hydrocarbons. The purified gases consist in their essential part of sulphurous acid which escapes through the pipe 33, and they are then collected and may be utilized for known purposes, particularly for the production of sulphuric acid.

956,010. Process of Manufacturing Gas. ADOLPH ZINDLER, New York, N. Y., April 26, 1910.

In the dry distillation of shales, peat, wood and all bituminous matter by the continuous process, it is usual to take the gases, by suction, from the different parts of the furnaces or retorts, but to conduct them collectively through one main to the cooling and purifying apparatus. In the gas-main the hot gases are mixed with comparatively cold gases, and it is well known that the latter are decomposed and deteriorated by the former.

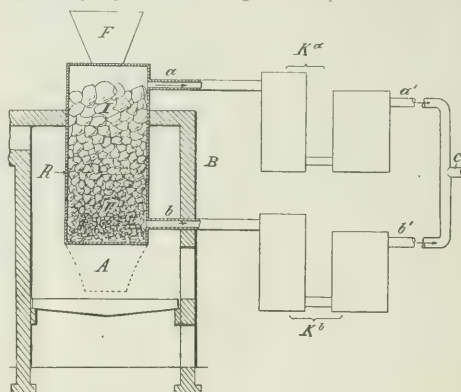
It is the object of this invention to prevent this deterioration.

The invention will be described in connection with the accompanying drawings.

The apparatus consists of a retort R provided with a filling hopper F and a discharge chute A. The retort R may be of any suitable construction, and may be a device of any suitable type other than that shown. This retort is heated externally by means of a furnace B. The fuel placed in the retort will as the gas is distilled pass downwardly and through the discharge chute A. This discharge chute is shown in dotted lines and may extend laterally and downwardly outside of the furnace so that the distilled fuel may be raked out. The gas as generated is drawn from the retort by means of a plurality of conduits or pipes *a*, *b*. These conduits connect with the retort at the upper and lower zones of different temperatures, that is, the lower zone is at a higher temperature than the upper zone. In the specific embodiment shown these zones of different temperatures are shown as upper and lower zones respectively. It is to be understood, however, that this invention is not limited to this specific embodiment, since any construction in which conduits connect with zones of different temperatures comes within the scope of this invention.

The gases derived from the different zones are independently passed through apparatuses  $K^a$   $K^b$ , which separately treat the gases. These apparatuses may be of any suitable form and may treat the gas in any suitable manner. In the specific con-

struction shown these apparatuses are each composed of coolers and scrubbers. The gases as they issue from these treating apparatuses may be utilized in any suitable manner. They may be kept apart and discharged into separate reservoirs or



holders, or they may be mixed and discharged into a common holder. In the specific embodiment shown, the gases issuing from the treating apparatuses through the conduits or pipes *a'*, *b'*, may discharge into a common main *c*, and hence may be utilized or discharged into a common holder.

The gases derived from zones of different temperatures in the retort are conducted away separately and treated separately before they are utilized or before they are mixed, where such mixture takes place. The decomposition of the cold gases by the hot gases is thus prevented. In this way the distillation of the tar regained from the colder derived from the zone of lowest temperature and the splitting up of this tar is prevented. In prior methods where the gases derived from zones of different temperatures—the tar, etc., from the separate gases which are of different qualities are mixed, thus necessitating fractional distillation to separate these different qualities. By separately treating the gases derived from the different zones, it is possible to obtain tar, etc., of different qualities, and therefore special and fractional distillation of the tar, etc., is obviated.



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## ORIGINAL PAPERS.

### THE USE OF FERRO-TITANIUM IN BESSEMER RAILS.

By P. H. DUDLEY.

The writer calculated and tested experimentally a formula for the use of ferro-titanium for Bessemer rails, to augment the average toughness and ductility of those of 0.50 in carbon and 0.096 in phosphorus, in connection with the New York Central Lines—1908 specifications. The use of Bessemer rails with practically 0.10 in phosphorus with as low carbon as mentioned under high-speed trains was not a matter of choice, but of stern necessity. It has been the expectation of Bessemer steel manufacturers and railroad officials for some years that owing to the exhaustion of the low phosphorus ores basic open-hearth rails would replace Bessemer, as the latter replaced iron less than half a century since. Several basic open-hearth plants have been installed and out of about 45,000,000 tons of rails in our tracks 2,000,000 tons are basic open-hearth. It was generally considered a simple problem to make the basic open-hearth rails of even 0.75 to 0.85 in carbon, but under 0.03 in phosphorus, and still secure immunity from rail fractures and failures, therefore, it was expected by the use of basic open-hearth rails that the fractures common to Bessemer steel would be eliminated.

The practical results of many fractures and failures in the new metal modified opinion and it will require time for a return to the conditions of manufacture which must be observed.

The chemical composition of 0.75 to 0.85 in carbon, with the accompanying manganese advocated at first as safe, forms in many cases a eutectic mixture in which the ferrite is apparently all absorbed, the ductility of the steel being low, hard and sensitive to shocks. The saturation point of the ferrite by carbon has been considered as 0.90, but in rails and tires with the manganese content it seems often ten to twenty points lower, and traces of cementite may occur. A carbon content of 0.62 to 0.75, with greater ductility, is considered more reliable in rails as girders.

The demand for basic open-hearth rails in 1907 and 1908 was far beyond the capacity of the plants to fill. Therefore, but few railroads were able to secure sufficient rails of that class of steel for their requirements and others had to be content with a small tonnage for trial. This compelled me to reinstate former Bessemer principles of practice which had been lost in the great demand for output, and also to try additional means for better Bessemer rails for modern heavy wheel loads and high-speed trains. I did not expect or consider that my method for the use of ferro-titanium would be generally used by the railroads for the Bessemer departments of all manufacturers were not so arranged that they could follow all the details but would be obliged to resort to more expensive methods.

The results of the first service tests seemed so satisfactory to other railroad systems that they wished to try similar rails and several trial orders were placed for 1,000 to 5,000 tons, distributed over a great extent of country. The rails passed through the unusually severe winter of 1909 and 1910 with favorable comparisons.

I have answered many inquiries in reference to my rails, but have been reluctant to answer requests for publication until I could have the results of the service of two winters to see whether or not they agreed and sustained the calculations and preliminary physical tests.

Five thousand tons of rails of the six-inch 100-lb. Dudley section were made in 1908 and sent to the Electric Division in New York City. These rails were laid in the autumn of 1908, and in May, 1910, not a single rail had broken. The plain Bessemer rails in the same section and location had heretofore

developed a number of fractures during the winters even for those having no higher content of carbon than the present rail in which ferro-titanium was used.

Seven thousand and five hundred tons of the same section were sent to the Boston and Albany Railroad and only three rails failed, two from injuries received in loading. While in three thousand tons of 80-lb. rails some of them laid in 1908, therefore, had two winters' service, not a rail fractured, which tends to corroborate the calculations and preliminary tests. The equally as good comparative results on other railroads beside the New York Central lines are further confirmation that some increase in purity, toughness and ductility of the metal has been practically secured.

The problem in the manufacture of rails for high-speed trains at the present time is to obtain a higher average purity, toughness and ductility for the metal of all the heats than was required fifteen and twenty years ago, before the advent of the present heavy wheel loads and high-speed trains. The five-inch 80-lb. rail which I first designed for the New York Central & Hudson River Railroad, in 1883, the phosphorus content was 0.08 with 0.45 to 0.50 in carbon. Some of these rails proved fragile in the track after a few years' service under the high-speed trains which were inaugurated after the introduction of that section. When I made the revised  $5\frac{1}{8}$  in. 80-lb. and six inch 100-lb. sections, and also the Boston & Albany 95-lb. section in 1890, I knew from experience that it would be necessary to increase the carbon content of those rails for heavy service. To do this I limited the phosphorus to 0.06 in the metal and made the carbon content 0.56 to 0.65 in the Boston & Albany 95-lb. and the 100-lb. rails. These proved under the drop test to be not only tough, but the ductility ranged from 10 to 14 per cent. as secured for the most of the heats.

To make and test the rails in 1891 I had to re-instate the drop test and made it a part of the specifications that 90 per cent. of the butts should stand a drop of 2,000 lbs. falling 20 feet, supports three feet apart, and heats of butts which broke, though gave four per cent. maximum elongation per inch, would be accepted. The butts before testing were stamped in the center on the base or head, as desired, with a spacing bar of seven conical points, each one inch apart. These six-inch former spaces after the drop would be extended and were measured by a flexible steel rule divided in hundredths of an inch, therefore, the excess hundredths per inch gave the percentage of elongation. The range of ductility of the steel was designed to be between 8 and 15 per cent., excepting the small percentage of heats of which the minimum elongation must be 4 per cent. or over to be accepted.

The maximum elongation per inch for the 100-lb.

rail under the 40,000 foot pounds of energy of the drop was only five per cent. for its standard permanent set of 0.92 of an inch. Therefore, most of the energy of the drop would be expended upon the butt when the four per cent. elongation was produced per inch before the butt broke or sheared.

A shear was not treated as a broken butt in the rejection of heats for the valuable indications it gave were that the upper limit in chemical composition for a fine textured steel had been practically reached. The elongations were measured and considered in accepting or rejecting the heats. It takes but a few minutes now to describe the earlier results in the heavier sections, but it was the work of years, first making the steel, rolling the sections, then taking yearly diagrams of the tracks by my Track Inspection Apparatus, and also studying the results of service for guidance in future work.

There were over 600,000 tons of the low phosphorus, 0.06, and high carbon rails made and in most of them the copper content ranged from 0.6 to 0.8 of one per cent., which, after the long service, is considered to have added to the toughness of the steel under the passing wheel loads as but a small percentage of the rails have broken after twelve to eighteen years of service. Since the exhaustion of the low phosphorus ores and the loss of the copper in the Bessemer rails for the same section, a greater decrease, proportionately, of the carbon has been required for the four additional points above 0.06, or 0.10 phosphorus in the metal. The minimum range of ductility for the higher phosphorus without copper must be six to seven per cent. instead of the former minimum of four per cent. with copper.

The high phosphorus content of 0.10 constitutes the greatest objection to-day to the use of such Bessemer rails for heavy traffic and is one reason why I am trying to make them better by the use of ferro-titanium.

Phosphorus makes steel brittle to shocks as it hardens it, which limits the carbon to about 0.50 for heavy sections, where they are to be used in temperatures which fall  $10^{\circ}$ – $20^{\circ}$  F. below zero in the winter months. The brittleness in the early Bessemer steel rails was attributed principally to the phosphorus content even with the low content of 0.30 to 0.40 carbon. It seemed to be erratic, or such effects were attributed to phosphorus, for it was found to exist in two or more forms in the steel, one form being considered harmless and another detrimental. This is not considered proven in practice, as all high phosphorus metal in rails has fractured more than low phosphorus Bessemer rails. The early sections of steel rails were rolled only  $3\frac{1}{2}$  inches to  $4\frac{1}{4}$  inches in height from small ingots and segregations of carbon and phosphorus were elongated and diffused more than is the case of heavier rails from large ingots.

Sections of 52-lb. rails, which were well under the light service, though some rails fractured, have been found recently which contained 0.14 and 0.16 phosphorus in two different brands of rails. These light sections had small mechanical properties, were flexible in the track and could not carry large bending moments, therefore there was more time to distribute the strains of the passing wheel loads through the metal of the section than there is in the present heavy stiff sections, carrying larger bending moments to reduce the undulations and train resistance of the track.

The first experiments of the use of ferro-titanium in the metal the ingots were better and the steel showed an increased purity, toughness and ductility. The same carbon content compared with the plain Bessemer steel in the same sections the ductility averages higher and runs more uniform for a larger number of heats than it has been possible to secure in ordinary Bessemer. The ferro-titanium as a subsidiary deoxidizer, besides reducing a greater percentage of oxides of iron in the steel, also reduces a portion of the nitrogen, which decreases the brittleness and thus adds to the toughness of the steel. The nitrogen content seems to be small in some heats, but higher in others, and by the use of ferro-titanium a more uniform range of ductility has been obtained in the steel.

The nitrogen content reported in some of the 1904 Bessemer rails which broke was 0.0147 to 0.0153, and in others which did not 0.003 to 0.006, according to determinations which I had made in 1906. These were considered as comparative indications rather than as accurate determinations which can now be readily and more cheaply made. It is considered as a working hypothesis that the nitrogen content in steel reduces the ductility five times faster than phosphorus and fifteen times faster than carbon in large sections of rails subjected to shocks. These comparisons will be checked for rectification as data is gathered in reference to nitrogen. The use of ferro-titanium shows a reduction of the nitrogen content in steel after its use and an increase in the toughness, besides a greater reduction of the oxides of iron.

Plotting the results of the elongation of the drop tests has been of invaluable service to me in rail manufacture for high-speed trains. The ductility of the steel in the full-sized section can be exhausted in two or more blows under the present Manufacturers' Standard Drop Testing Machines, the butts being stamped in inches before testing, as already described. The elongation of the metal under the drop testing machine compares favorably with that obtained by static loads in the testing machine. The tendency is an increase of possibly two or more per cent., owing to the fact that the base of the rail which

stretches does not neck as in the case of a tensile specimen. It is also probable that the energy converted into heat, and the rising temperature of the butt, under successive blows, slightly increases the ductility of the metal. The possibility of determining quickly the ductility of the metal in the section from hour to hour as rolled is one of great value, as conditions of manufacture can be followed as they occur.

A 100-lb. rolled section of pure iron, before exhaustion of ductility, would show under the drop an elongation of 45 or 50 per cent. for two or three inches directly under the point of impact. By adding carbon and manganese to the iron, increasing the physical properties of the metal, there is, as expected, a reduction in the elongation of the metal. The content of impurities of phosphorus, sulphur, nitrogen, arsenic and oxides that will make further reductions of elongation and should be considered in the chemical composition for service as girders or to harden the metal to resist abrasion for slow trains.

Fig. 1 shows a chart of the records plotted of the drop tests of 224 heats of 90-lb. Bessemer rail A. S. C. E. Section, rolled in March, 1910. The horizontal lines on the charts with their figures indicate

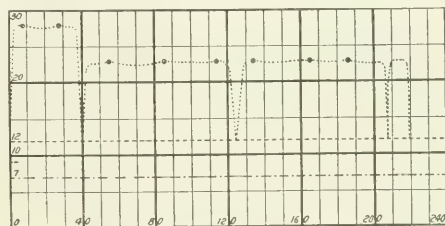


Fig. 1.—Consecutive drop tests.  
90-lb. Rails, A. S. C. E. Section.  
Bessemer, C. 0.41, Mn. 0.60, P. 0.05, Si. 0.13

the percentages of the elongation and ductility while the vertical lines and figures the heat numbers. The chemical composition of the steel averaged 0.44 in carbon and 0.096 in phosphorus, the manganese being nearly one per cent. These rails were intended for a high average range of ductility as girders and therefore are on the soft side for wear.

The maximum elongation per inch under the drop of 2,000 lbs. falling 17 feet was 7 per cent. The elongation for a single blow for all the heats is definite, for each butt withstood the drop and retests were not required in a single case. This percentage is shown by a line of dashes and dots marked 7 per cent. Therefore, the minimum ductility of every heat is above the 7 per cent. line. There were thirteen of the butts distributed through the heats and the ductility exhausted completely to find the maximum for the metal. These are plotted on the charts by a line of dots with circles, the latter to indicate the heats which were tested.



It is not possible in regular work of the mill to have the drop testing machine sufficient time to exhaust the ductility in every heat, but only of a few to show the elongation in the general run of the steel. It is probable that there would be some heats which were not exhausted completely that the minimum ductility would be less than the 12 per cent. shown for the five heats, but it would be above 7 per cent.

Each of the five heats, beside standing the first blow, required a second to break them, the elongation being about 12 per cent. and is shown by a horizontal line of short dashes. The two circles in the first group of 40 heats indicate there were two tests which required five blows to exhaust the 28 per cent. ductility, and then a heat broke under two blows with the 12 per cent. elongation. Three butts in each of the following groups of 80 heats also gave 23 per cent. ductility. The following 15 heats are represented by two butts which broke at the second blow, but each gave about 12 per cent. elongation.

The plotting of the group in this manner is to obtain a general indication of the elongation and ductility during a turn of twelve hours, or two turns in twenty-four hours' work, and this is above the average for Bessemer rails.

The charts of the drop tests plotted in this manner show positively the ductility of every heat secured by one blow of the drop, and of the others in which the ductility is completely exhausted. While the permanent sets under the drop have been recorded, it has not been usual to measure the elongation of the metal per inch in the section except in my practice.

To compare the ductility of individual heats or melts, tests are made exhausting the ductility by two or more blows. These are shown by Figs. 2 to 7, inclusive. The graphic representation of each heat of melt in the figures is shown, as will be seen, from the percentage marks per blow and are represented by vertical lines of about one-fortieth of an inch ( $1/40''$ ) in thickness; two blows double that thickness; three blows three times; and four blows by one-tenth of an inch ( $1/10''$ ). The different steps shown on the chart gives the percentages of ductility obtained at each blow, while a double width of the top indicates that another blow was required to break the butt, though additional elongation was not produced. The horizontal lines in the diagrams with their figures indicate the percentages of elongation.

Fig. 2 shows elongation and ductility tests of plain Bessemer steel rolled June 14 and 15, 1909. The heats Nos. 14793 and 14925, represented by the first and second graphs, were tested March 28, 1910, drop 17 feet. The steel was intended for a range of ductility of 10 to 15 per cent. and required three blows of the drop to break the butts.

The heat No. 31703, represented by the third graph, was rolled September 18, 1909, and tested March 28, 1910, drop 17 feet. The object of holding these butts was to see about the removal of the initial

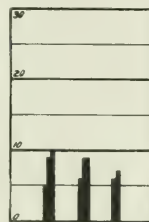


Fig. 2.—Ductility tests.  
100-lb. rails, Dudley Section.  
Bessemer: C, 0.50; Mn, 1.00; P, 0.056; Si, 0.13.

strains of rolling after six to eight months of manufacture. The butts were reserved on skids under cover at the mill but had not been handled. It had been noticed several times that groups of butts which stood the drop test on the day of manufacture or a day thereafter, that when some were laid aside on the ground four or five weeks they did not stand the drop test, but some of the same butts, after three to six months, usually stood the test, the belief being that the initial strains of rolling had by time become better equalized. I cite this as a coincidence which occurred with the author twice, and others have had similar coincidences, but these do not establish a general law, as the manner of storing is now believed to be an important factor.

New steel rolls, after turning to dimensions, are safer from breaking by "seasoning" six to eight months before using, for a large amount of metal has been removed from the exterior diameter and the interior strains require time or change of temperature to become equalized.

Fig. No. 3: Heat Nos. 17571 and 17575, represented by the first and second graph, were rolled June 1, 1909, for the Detroit River Tunnel Co. These had a discard of 19 per cent. and were tested March 29, 1910. The third graph was the same

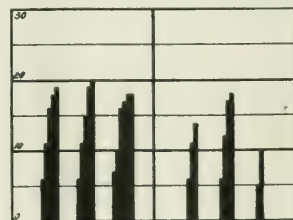


Fig. 3.—Ductility tests, 100-lb. rails.  
F. T. Bessemer: C, 0.50; Mn, 1.00; P, 0.055; Si, 0.13.

section rolled May 1, 1909, but tested the same date as the others. These were ferro-titanium rails to have a range of 15 to 20 per cent. ductility. Height

of drop 17 feet. The section was the A. S. C. E. 100-lb.

It did not make any difference when these butts were tested, they proved tough and at any time requiring five blows for the first two and six for the third, which was a 9 per cent. discard three-rail ingot. The other two ingots were from the same molds but three-rail ingots with more discard.

Graphs fourth and fifth show the B and C rails of heat No. 39926. The B rail required three blows to break and had 14 per cent. ductility. The C rail required four blows and had a ductility of 18 per cent. These were 100-lb. rails with a chemical composition to have a range of 10 to 15 per cent. ductility. The sixth graph was a condemned A rail for a blistered web. The ingot was delayed in charging into the reheating furnace until a large shrinkage cavity formed and the section failed the second blow from mechanical weakness, due to the shrinkage cavity. It stood the one required blow, therefore would not have been detected except for the blistered web. Any interruption to the regular mill practice as an

the change from a medium rolling temperature to one a few degrees lower, by a reduction of ductility, though in none of the examples below the safe limit of 10 per cent. elongation and required two blows to break the butts. Fig. 5, shows heats of plain Besse-

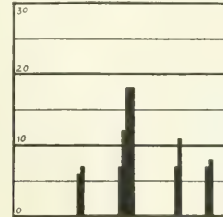


Fig. 5.—Ductility tests.  
100-lb. rails, A. S. C. E. Section.  
Bessemer: C, 0.50; Mn, 0.98; P, 0.06; Si, 0.13.

mer steel in 100-lb. rails intended for a range of 10 to 15 per cent. ductility. Two of the heats gave only 7 and 8 per cent. elongation under two blows each, a third 11 per cent. elongation for the second blow, while one heat gave 18 per cent. elongation and required four blows to break the butt. These were nearly consecutive heats and show quite a range in the ductility often observed in plain Bessemer steel.

Fig. 6 shows the elongation and ductility of 100-lb. New York Central rails, Dudley 6-inch 100-

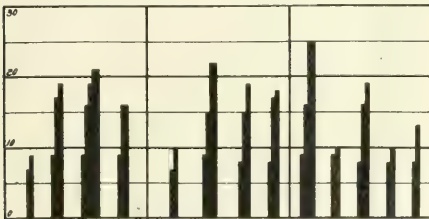


Fig. 4.—Ductility tests.  
5 1/2-inch 80-lb. rails, Dudley Section.  
F. T. Bessemer: C, 0.49; Mn, 0.96; P, 0.06; Si, 0.13.

ingot car off the track, a "sticker" at the "stripper," or an extra run to the gantry, will affect the setting of an ingot or a heat of ingots, more decidedly the greater the purity of the steel.

Fig. No. 4 represents the Dudley section of 5 1/8 inch 80-lb. rails, rolled from four-rail length ingots which are about 350 lbs. heavier than the three-rail length for the 100-lb. rails, while the chemical composition is practically the same, the range of ductility being only 10 to 15 per cent. to resist curve abrasion. Ferro-titanium raised the minimum ductility by three to four per cent. in these rails.

The heat No. 8704 shown by the first graph was condemned by the maker on account of being too high in carbon, yet it shows 9 per cent. of ductility. It would have been an excellent rail to resist abrasion upon curves under slow traffic. The other twelve heats from No. 16195 to 16224 were all rolled March 29, 1910, and tested April 14th. The lowest range is 10 per cent. ductility, while the majority show over 18 per cent., one heat showing 25 per cent., all heats requiring two or more blows of 16 ft. to exhaust the ductility. This wide range is interesting and reflects



Fig. 6.—Ductility tests.  
100-lb. rails, Dudley Section.  
F. T. Bessemer: C, 0.50; Mn, 1.00; P, 0.06; Si, 0.13.

lb. section. These were designed for a range of ductility of 10 to 15 per cent. All of the heats required three blows to exhaust the ductility and none broke under 11 per cent. elongation.

Fig. 7 shows a number of heats of open-hearth

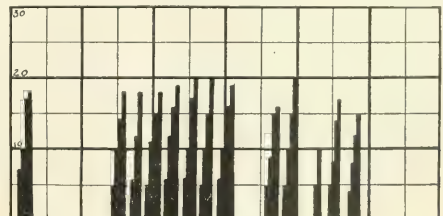


Fig. 7.—Ductility tests.  
100-lb. rails, A. S. C. E. Section.  
B. O. H.: C, 0.68; Mn, 0.86; P, 0.02; Si, 0.10.

rails with carbon about 0.69 with the phosphorus under 0.03. These were intended for a range of ductility of 12 to 18 per cent. for use under high-speed trains where the temperature in winter falls 10 to 30 degrees F. below zero. Rails of similar composition have been in service three and four years with comparatively few fractures.

#### *Correlation of the Equipment and the Tracks.*

The equipment and track are of necessity so intimately correlated that for high-speed trains of heavy loads the wheels need tires of higher physical properties and maintenance than formerly required. The tires under the heavy wheel loads do not all wear uniformly the entire circumference of the tread, soft spots developing in a portion and the wheels become eccentric, increasing the dynamic shocks upon the rails each revolution. The metal in tires under the heavy loads and high-speed trains is more severely strained and abraded than in the past, and it will require as thorough consideration of the comparative methods of manufacture as has been exercised for rails.

The tonnage upon the tread of a tire accumulates with great rapidity. The 36-inch wheel makes 560.2 revolutions per mile, therefore, every portion of the metal of bearing surface of the tread is subjected to its static load 560.2 times per mile, and for a static load of five tons it would be equivalent to 2,801 tons per mile, beside the generated wheel effects.

The accumulated tonnage exclusive of the generated wheel effects for a static load of five tons per wheel in a trip from Boston to Chicago would be 2,865,423 tons; New York to Chicago, 2,700,164 tons; New York to St. Louis, 3,243,558 tons; New York to Cincinnati, 2,478,885 tons. A tender wheel with an average static load of nine tons, or 5,041.8 tons per mile, the tonnage for a trip of 150 miles would be 756,270 tons and run in about three hours and fifteen minutes. The generated wheel effects would be from 20 to 50 per cent. additional in all cases, depending upon how smooth or even the treads maintained their circumference, speed, and also the smoothness of the track. A tender wheel became eccentric for a space of about ten inches in the tread after it had run 29,000 miles and its total tonnage approximated 146,000,000 tons in about six months' service. Some tires become eccentric after running 10,000 to 15,000 miles. The tires are subject to greater tonnage than rails in a given length of time. Years are required for the rails to carry as heavy tonnage as the tires do in a few months, the latter being returned for further duty. It requires a metal of high elastic limits of the steel to sustain the treads without undue wear.

#### CONCLUSIONS.

##### 1. The illustrations of the elongation and ductility

tests indicate the possibility that from a well studied chemical composition for steel rails with good fabrication a range of ductility in reference to great toughness can be prescribed for the different sections to meet conditions of service as girders for high speeds, or with more hardness but less ductility, to resist curve abrasion and wear at slow speeds.

2. Rails which are to be used in low temperatures under high-speed trains the toughness and ductility of the metals must have preference over hardness, particularly of that high in phosphorus, as the latter limits the amount of carbon which can be used to resist abrasion and wear, and still be safe as girders.

3. The carbon in basic open-hearth rails should be below the eutectic mixture of the chemical composition for high-speed trains, as otherwise the toughness and ductility may be reduced to a condition of brittleness in many rails.

4. The average ductility in Bessemer rails of 0.50 carbon and 0.095 in phosphorus has been raised two or three per cent. by the use of ferro-titanium in the steel as practically shown by one and two winters' service, and is considered worthy of further trials.

Ferro-titanium has a direct action upon the purification of the metal and setting of the ingots, and must, therefore, be used with a knowledge of what is desired, to secure the best results.

5. The problems of rail-making for service in the United States are now upon a better basis than ever before, owing to the coöperation of the railroad companies and the manufacturers to secure rails which are suitable for the present traffic.\* This arises from a more general knowledge of what is required than was understood a few years since.

[CONTRIBUTION FROM PITTSBURGH LABORATORY, TECHNOLOGIC BRANCH, UNITED STATES GEOLOGICAL SURVEY.]

#### SOME VARIATIONS IN THE OFFICIAL METHOD FOR THE DETERMINATION OF VOLATILE MATTER IN COAL.

By A. C. FELDNER and J. D. DAVIS.<sup>1</sup>

Received May 13, 1910.

In view of the proposed revision of the official methods of coal analysis, it may be of interest to present certain experimental data bearing on the present official method for the determination of volatile matter in coal.

These experiments were conducted in the Pittsburgh and Washington laboratories of the U. S. Geological Survey, primarily to ascertain the difference in volatile matter produced by using a 20 cm. natural gas flame as compared with the 20 cm. coal gas flame. After starting the work it was found desirable to investigate the influence of other factors such as gas pressure, type of burner, and surface condition of

<sup>1</sup> Presented by permission of the Director, U. S. Geological Survey.



platinum crucible, *i. e.*, dull gray or polished. In order to eliminate influence of variation in size and shape, three 30-gram platinum crucibles of practically the same capacity and weight with closely-fitting covers were used in all the experiments, it having been demonstrated by actual trial that each one of the three crucibles gave the same results.

As these crucibles had been regularly used for volatile determinations, both inner and outer surfaces had the dull gray appearance which platinum assumes when heated several times in the natural gas flame. To protect the flame from air currents, the platinum triangle supporting the crucible was enclosed in a cylindrical sheet metal shield, lined with asbestos, 15 cm. long and 7 cm. in diameter, the platinum triangle being placed 3 cm. below the top of the shield; the bottom of the crucible was exactly 8 cm. above the mouth of the burner.

The temperature measurements were taken on a parallel test, using the same crucible with the regular cover replaced by one of nickel; the thermocouple, inserted through a small opening in the cover, was placed 2 mm. above the bottom of the crucible; the opening around the thermocouple leads was closed with a cement of barium sulphate and sodium silicate.

The description of coals tested is given in the following table:

Coal No.	Type.	Locality.
1	Semibituminous	Pocahontas, W. Va.
2	"	" "
3	"	" "
10	"	" "
11	"	" "
12	"	" "
4	Bituminous	Pennsylvania
5	"	"
6	"	"
7	Anthracite	"

*Influence of Change in Gas Pressure.*—Coal gas can be burned efficiently at low pressures, two to three inches of water being sufficient; natural gas, owing to the much larger proportion of air required, must be supplied to the burner at higher pressures.

Table II gives results obtained by varying the pressure from 1 to 13 inches of water:

TABLE II.—INFLUENCE OF GAS PRESSURE ON VOLATILE MATTER.  
Natural gas; Tyrell burner; 20 cm. flame.

Gas pressure in inches of water.	Per cent volatile matter.			Maximum temperature, °C.	Kind of flame.
	Coal No. 1.	Coal No. 3.	Coal No. 6.		
1	15.4	15.8	32.4	760	Yellow tipped
2	15.2	16.7	...	...	...
3	15.4	16.7	32.3	780	Faint yellow tip
4	16.3	...	32.7	...	...
5	16.7	16.5	32.6	800	Yellow tip just removed
6	17.2	16.7	33.0	...	Long inner cone
8	16.7	...	32.7	...	...
9	...	17.2	...	825	Well defined inner cone
12	17.2	16.9	32.7	...	...
13	17.1	17.1	32.5	845	Sharp, greenish, inner cone

Temperature during volatile determination on coal No. 1 with varying pressures. (Time in minutes.)

Pressure in inches of water.	0.5 °C.	1 °C.	1.5 °C.	2 °C.	2.5 °C.	3 °C.	3.5 °C.	4 °C.	4.5 °C.	5 °C.	6 °C.	7 °C.
1	180	450	590	670	725	745	750	755	760	760	760	760
3	185	440	590	670	740	760	770	780	780	780	780	780
5	180	450	605	710	765	790	800	803	803	802	800	800
9	220	480	635	720	775	805	815	820	820	823	823	823
13	320	550	690	780	825	840	848	848	848	848	847	845

The maximum temperature varies from 760 to 845° C. Coal No. 6, a bituminous coal, gives practically the same yield of volatile matter throughout the series. The semi-bituminous coals, Nos. 1 and 3, are more sensitive to variations in temperature, the extremes being nearly 2 per cent. The maximum pressure, 13 inches, was used in all subsequent work with natural gas.

It has frequently been noted by the writers that during the early part of the 7-minute volatile process, the coke swells or puffs up to the lid of the crucible, oftentimes raising it slightly. On comparing such determinations with duplicates that did not swell, they were invariably found to be one to two per cent. lower in volatile matter. This peculiar swelling has been noticed only in the case of semi-bituminous coals. It is more apt to happen at the lower temperatures, and when the coal is kept perfectly level in the bottom of the crucible. The swelling can be prevented by simply tapping the crucible on one side so as to settle the coal in an inclined position across one corner of the bottom of the crucible, thus preventing the formation of a film of fused coal across the crucible. Comparative results are given in the following table:

TABLE III.—VARIATIONS DUE TO SWELLING OR PUFFING UP OF COKE IN CRUCIBLE.

Coal No.	Coke residue in compact lump in bottom of crucible.	Coke residue swelled half way to cover.	Coke residue swelled up to cover.
1	16.7	16.2	15.3
	17.2	16.8	14.8
	17.1	16.0	15.2
	...	15.8	15.1
	...	15.7	15.7
	...	...	15.6
2	Average, 17.0	16.0	15.3
	17.0	15.4	15.4
	16.9		

*Influence of Type of Burner.*—It is reasonable to expect some lack of uniformity in volatile results where widely different types of Bunsen burners are used. A burner with a large bore will give a larger flame volume, with a correspondingly increased heating effect. Determinations were made with the following types of burners on both natural and coal gas:

- The simple Bunsen burner, bore 9 mm.
- The Tyrell<sup>1</sup> burner, bore 9 mm.
- The Fletcher, No. 5g, burner, bore 12 mm.

<sup>1</sup> Eimer & Amend catalog, p. 80.

The results are given in Table IV.

TABLE IV.—INFLUENCE OF DIFFERENT TYPES OF BURNERS.

Coal No.	Per cent. volatile.			Difference.	
	Fletcher.	Tyrell.	Bunsen.	Fletcher and Tyrell.	Fletcher and Bunsen.
(a) Natural gas.					
1	17.2	17.0	15.7	-0.2	-1.5
2	17.0	16.8	15.8	-0.2	-1.2
6	32.8	32.6	32.6	-0.2	-0.2
4	31.8	31.3	31.2	-0.5	-0.6
5	31.5	31.5	....	0.0	...
Average.				-0.2	-0.8
Temp. °C. 850° 850° 790°					
(b) Coal gas (Pittsburg).					
1	17.0	16.7	16.3	-0.3	-0.7
6	33.0	32.3	....	-0.7	...
5	31.7	31.4	....	-0.3	...
Average.				-0.4	...
Temp. °C. 855° 810°					
(a) Carburetted water gas (Washington).					
1	18.3	....	17.2	....	-1.1
11	18.6	....	17.8	....	-0.8
12	18.0	....	17.7	....	-0.3
10	18.7	....	18.4	....	-0.3
3	18.8	....	18.5	....	-0.3
2	18.2	....	17.6	....	-0.6
Average.				-0.6	...
Temp. °C. 970°					

TABLE V. TEMPERATURE MEASUREMENTS. (°C.)

20 cm. flame; natural gas at 13 inches water pressure.

Time in minutes.	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	6	7
Fletcher burner.												
coal. No. 1.....	280	590	710	788	830	845	850	850	850	850	850	850
Tyrell burner, coal												
No. 1.....	250	530	670	780	825	840	850	850	850	850	850	850
Bunsen burner, coal												
No. 1.....	250	580	700	760	780	785	785	790	790	790	790	790
Pittsburg coal gas at 2.5 in. pressure; 20 cm. flame.												
Tyrell burner, coal												
No. 1.....	260	540	680	760	810	835	850	855	855	855	855	855
Washington illuminating gas at 2.5 in. pressure; 20 cm. flame.												
Fletcher burner.												
Coal No. 1.....	630	...	910	...	975	...	975	...	970	970	970	970

The Fletcher burner gives slightly higher volatile matter than the Tyrell with practically the same maximum temperature. The larger flame volume of the Fletcher burner, heats up the crucible more rapidly, which increases the gas yield slightly. With the use of natural gas, the maximum temperature of the Bunsen burner is 60° less than either the Fletcher or Tyrell; this produces a marked difference in volatile matter in the case of the semi-bituminous coals. Evidently a burner like the Fletcher or Tyrell, admitting of both gas and air regulation, is preferable to the simple Bunsen.

*Influence of Composition of Gas.*—In order to determine the influence of composition of fuel gas, determinations were made over 20 cm. coal gas flame and 20 cm. natural gas flame, each gas being supplied to the burner at its proper pressure.

The natural gas analyzed as follows:

Carbon dioxide.....	0.1
Paraffin hydrocarbons.....	98.6
Nitrogen.....	1.3

100.00

The coal gas<sup>1</sup> analyzed:

Unsaturated hydrocarbons.....	7.5
Carbon dioxide.....	1.5
Oxygen.....	0.2
Carbon monoxide.....	8.9
Methane.....	44.8
Hydrogen.....	33.7
Nitrogen.....	3.4
100.00	

Both series of volatile determinations were made by the same analyst, using the same apparatus, the only difference being in the fuel gas used. The results are shown in Table VI:

TABLE VI.—DIFFERENCE DUE TO USING NATURAL OR COAL GAS.

	Per cent. volatile.		
Coal No.	Coal gas, 2.5 in. pressure.	Natural gas, 13 in. pressure.	Difference
(a) Fletcher burner.			
1	17.0	17.2	+0.2
2	17.1	17.0	-0.1
6	33.0	32.8	-0.2
4	31.5	31.8	+0.3
5	31.7	31.5	-0.2
Average.			0.0
(b) Tyrell burner.			
1	16.7	17.0	+0.3
6	32.3	32.6	+0.3
4	31.6	31.3	-0.3
5	31.4	31.5	+0.1
7	4.5	4.3	-0.2
Average.			+0.04

Temperature °C., 855°

850°

The temperatures are practically the same and the variations in volatile matter average zero. It should be noted, however, that the natural gas was supplied to a carefully regulated burner at 13 inches pressure. If the comparisons were made at the lower pressures usually found in laboratories, the results by natural gas would be decidedly lower.

Table VII gives a comparison of volatile matter obtained on the same samples of coal, in two different laboratories of the Geological Survey. The Pittsburg laboratory used natural gas at 13 inches water pressure with a Tyrell burner; the Washington laboratory used illuminating gas at 2 inches pressure with the Fletcher burner. The height of flame was 20 cm. in each case:

TABLE VII.—COMPARISON OF RESULTS OBTAINED IN DIFFERENT LABORATORIES.

Coal No.	Per cent. volatile matter.		Difference.
	Pittsburg. Natural gas, 13 in. pressure. Tyrell burner.	Washington. Illuminating gas, 2.5 in. pressure. Fletcher burner.	
1	17.0	18.3	+1.3
2	16.8	18.2	+1.4
3	17.0	18.8	+1.8
4	31.3	32.5	+1.2
5	31.5	32.6	+1.1
6	32.6	33.4	+0.8
7	4.3	5.3	+1.1
10	17.7	18.7	+1.0
Average.			+1.2

Temperature 850° C.

970° C.

<sup>1</sup> Coal gas taken from the mains of the gas company that supplies artificial gas, in Pittsburg, Pa.

From the previous experiment on natural and coal gas, closely agreeing results would be expected. Such, however, was not the case. As shown in the table, the Washington series averaged 1.2 per cent. higher than the Pittsburg. The maximum temperature of 970° C., noted in the Washington laboratory, was 120° higher than noted with either coal or natural gas at the Pittsburg laboratory. It had been supposed that the Washington illuminating gas was of a similar composition to that of the Pittsburg coal gas. This assumption, however, proved to be erroneous, as shown by the following analysis:

TABLE VIII.—ANALYSIS OF WASHINGTON ILLUMINATING GAS

	Per cent.
Carbon dioxide .....	3.0
Unsaturated hydrocarbons.....	10.4
Oxygen.....	1.0
Carbon monoxide.....	27.6
Methane.....	19.0
Hydrogen.....	33.1
Nitrogen.....	5.9
	100.0

The Washington gas consists entirely of carburetted water gas. It contains 26 per cent. less methane and 19 per cent. more carbon monoxide than coal gas. The replacement of methane by carbon monoxide decreases the flame volume very materially, and since the height of flame is the same in both cases, the heating effect of a low methane gas is, under ordinary laboratory conditions, considerably greater.

Chikashiga and Matsumoto<sup>1</sup> call attention to the disadvantages of uncarburetted water gas as a laboratory fuel on account of the high temperature of the flame produced. They state that "comparatively thick copper wire and sheet, and even thin platinum wire, are easily melted and hard glass easily worked in its flame."

Another factor that may have contributed to the difference in temperature noted in the two laboratories is the surface condition of the platinum crucible. Constam, in a paper<sup>2</sup> communicated to the Seventh International Congress of Applied Chemistry, mentions "that the slower rise and the lower final temperature in dull platinum crucibles caused the yield of coke in them to be greater than in polished platinum crucibles."

As the crucibles used in all the experiments at the Pittsburg laboratory were very dull and tarnished in appearance, it was decided to polish them and then run some determinations to check Constam's conclusions. The results are given in Table IX:

TABLE IX.—COMPARISON OF VOLATILE MATTER PRODUCED IN THE SAME CRUCIBLE BEFORE AND AFTER POLISHING.

Coal No.	Per cent. volatile.		Difference.
	Before.	After.	
10	17.0	18.1	1.1
3	17.0	18.1	1.1
6	32.6	33.3	0.7
Temperature °C.	845°	890°	45°

<sup>1</sup> Jour. Soc. Chem. Ind., 23 (1904), Jan. 30, p. 50.<sup>2</sup> Jour. für Gasbel. (1909), Oct. 9, p. 889.

Temperature measurements. (°C.)

Time in minutes	0	5	1	15	2	25	3	35	4	45	5	6	7
Before polishing, coal													
No. 1.....	250	530	670	780	825	840	848	850	850	850	850	850	850
	320	550	690	780	825	840	848	848	848	848	848	847	845
After polishing, coal													
No. 1.....	240	590	750	840	880	890	890	890	890	890	890	890	890

TABLE X.—VOLATILE MATTER BY DISTILLATION

Test	Time in minutes.	Vacuum.	Per cent. volatile moisture.	Remarks.
1	30	3/4-in. Hg	18.3	Retort weighed.
2	45	3/4-in. Hg	18.7	Coke weighed.
3	45	3/4-in. Hg	19.4	Coke weighed.
4	45	3/4-in. Hg	18.2	Coke weighed.
5	40	4-in. H <sub>2</sub> O	18.8	Coke weighed.
6	45	Atmospheric pressure	18.7	Gradual heat.
		Average.	18.7	
7	7	Atmosphere of CO <sub>2</sub>	18.5	30-gram platinum crucible heat treatment as in official method.
8	7	Atmosphere of CO <sub>2</sub>	18.3	
9	7	Atmosphere of CO <sub>2</sub>	18.6	
		Average.	18.5	
		Official method.	19.3	

In tests Nos. 1 to 6, inclusive, a sample of Pocahontas coal was subjected to destructive distillation in an iron retort, made from a piece of 1-in. gas pipe, capped at one end and tubulated at the other. The retort was heated by means of a train of Bunsen burners to a bright red heat, in a furnace of asbestos board. A 20-gram charge was used.

Tests Nos. 7 to 9, inclusive were made in a 30-gram platinum crucible with a tubulated cover; carbon dioxide was kept passing through during the determination; the heat treatment was exactly the same as in the official method. Both retort and crucible tests give results somewhat lower than the official method, although not materially.

## SUMMARY.

The results of these experiments may be briefly summarized as follows:

Two laboratories are likely to vary 2 per cent. in volatile matter, both using the official method. The percentage of volatile matter obtained from the same sample of coal varies with the temperature and rate of heating. This is not sufficiently defined by height of flame. Temperatures ranging from 760° C. to 890° C. may be attained with a 20 cm. natural gas flame, when the gas pressure is varied from 1 to 13 inches of water; variations of 2 per cent. volatile matter are thus produced. Difference in type and size of burner influence results from 0.3 to 1.5 per cent.

Polished crucibles become hotter and yield about 1 per cent. more volatile matter than dull gray ones.

Laboratories using natural gas are apt to get results on volatile matter that are considerably lower than those using coal gas, unless the following precautions are observed:

(1) Gas should be supplied to the burner at a pressure of not less than 10 inches of water.



(2) Natural gas burners admitting an ample supply of air should be used.

(3) Gas and air should be regulated so that a flame with a short, well-defined inner cone is produced.

(4) The crucibles should be supported on platinum triangles and kept in well-polished condition.

## LABORATORY METHODS FOR ORGANIC NITROGEN AVAILABILITY.

By C. H. JONES.

Received February 17, 1910.

There is an extensive demand for nitrogen in a form suitable for plant food. This demand has been mainly supplied in the past by nitrate of soda, sulphate of ammonia, and the animal and vegetable ammoniates, including dried blood, various tankages, fish scrap, bone meal and cottonseed-meal. These constitute a class which furnish nitrogen to the growing plant in a readily available form.

As a supplement to these high-grade manures there has gradually come into use another group of nitrogen-containing materials including raw and treated leather, peat, tartar pomace, garbage tankage, mola meal, beet and gas-house refuse, and others. Their nitrogen availability is supposed to be considerably less than obtains with the so-called standard ammoniates, the nitrogen being so "locked up," "fixed," "embalmed" or "inert" that decomposition in the soil is a long, slow process. Most fertilizer laws legislate against materials in this class, prohibiting their use unless statement of their presence is made.

It does not follow that because a popular classification puts a material in the inert class, that the material may not, by suitable treatment, be so changed as to merit a place in the readily available nitrogen group. The personal equation must be eliminated and each material allowed to stand on its own merits as measured by careful field and pot experiments. In other words, the true availability of any source of nitrogen for plant food must be eventually determined by the growing plant.

It happens, unfortunately, that field and pot experiments cannot be conducted without extensive equipment, that they are time-consuming, and that the great variation in results under seemingly uniform conditions, with different crops, soils, etc., necessitates repetition if anything like true availability averages are to be secured. This has led to the formulation of short laboratory methods designed to differentiate between ammoniates of high and low crop producing power. A history of suggested methods is beyond the scope of this paper and would be out of place here.<sup>1</sup>

I wish to describe at this time first the alkaline

permanganate method and second the pepsin digestion method as employed in the Vermont Experiment Station laboratory and submit results obtained by their use on fifty-one samples representing many so-called high- and low-grade animal and vegetable ammoniates now on the market.

*The Alkaline Permanganate Method.*—Weigh out an amount of sample containing 0.045 gram of organic nitrogen and transfer to a 600 cc. distillation flask. Add 100 cc. of alkaline permanganate solution (16 grams of pure potassium permanganate and 150 grams sodium hydroxide dissolved in water and made to volume of 1 liter), connect with a condenser to which a receiver containing standard acid has been attached, and digest below the boiling point for 30 minutes. Then boil until 85 cc. of the distillate are obtained. If the material shows a tendency to adhere to the sides of the flask, an occasional gentle rotation is necessary during distillation.

*Pepsin Digestion Method.*—Weigh out an amount of sample containing 0.025 gram of organic nitrogen. With raw materials transfer to a suitable 150–200 cc. flask and add 100 cc. of a pepsin-hydrochloric acid solution. Digest for 24 hours in a water bath at a constant temperature of 40° C., keeping flasks loosely corked. At the end of the 2nd, 5th, 8th, and 11th hours, add 2 cc. of 10 per cent. hydrochloric acid solution. Shake well after each acid addition. After the digestion filter the contents of the flask through single filters and wash until filtrate amounts to 400 cc. Dry and determine nitrogen in the residue by the Kjeldahl or Gunning method.

With commercial fertilizers weigh the required amount on a filter, wash with about 200 cc. water, and treat residue as already described.

The pepsin-hydrochloric acid solution is prepared by dissolving 5 grams of the Armour & Co. soluble scale pepsin (1 : 3000 U. S. P.) in 1000 cc. of two-tenths per cent. hydrochloric acid.

In using this permanganate method with commercial fertilizers it is necessary that the nitrogen present as ammonia and as organic nitrogen be first determined. The amount of material taken is based on the percentage of organic nitrogen present. Nitrates are unaffected by the treatment, and any ammonia originally present in the sample is deducted from the result obtained before calculating the organic availability. Both nitrates and ammonia are given due credit under the total availability column.

In testing the availability of commercial fertilizers, particularly when ammonia salts are present, it is recommended that the water-insoluble organic nitrogen be determined. An amount of material equivalent to 0.045 gram of water-insoluble organic nitrogen is then weighed onto a hardened filter, washed with about 200 cc. of water (small portions at a time), the residue dried at about 90° C. and transferred from the filter

<sup>1</sup> Vt. Station, *Rep.*, 11, 1897, page 160.

into the distillation flask. Permanganate solution is then added and the distillation continued as usual.

The alkaline permanganate method has been used on every sample of officially collected commercial fertilizer analyzed in Vermont since 1898. By its use we have noted many variations in nitrogen source from year to year in standard brands, due to changes in company management and other causes. A comparison of the results by both company averages and on individual samples during this interval of 12 years is a long but exceedingly interesting study in itself. Such results as run below 50 per cent. by the permanganate method are tested by the pepsin method outlined above for a further insight as to the nature of the organic nitrogen present.

This permanganate method has been criticized chiefly in that it fails to do justice to cottonseed meal and that concordant results are not obtained by different analysts. The first objection is admitted and the reasons therefor have been elsewhere explained.<sup>1</sup> Inasmuch, however, as in certain sections cottonseed meal rarely, if ever, appears in commercial fertilizers, and knowing that the time-honored pepsin method does ample justice to this and similar vegetable ammoniates, it should not exempt the local use of the alkaline permanganate method if circumstances warrant. Concerning the second objection, the writer would state that from an experience covering twelve years he is convinced that non-agreement over certain limits is due primarily to details of manipulation. In this laboratory upright condensers are used and the end of the condensing tube does not dip into the standard acid. Working with commercial fertilizers our variation between parallels is usually not to exceed 0.10 per cent. nitrogen, equivalent to an availability of about 2 per cent. With certain concentrates the variation may run a little higher but a few duplications will soon afford a satisfactory average. It should be remembered that we are not comparing availability differences of from 2 to 4 per cent. Thus, if two different brands show availabilities of 64 and 66 per cent., respectively, they both rank equally well, but if one shows 40 per cent. and the other 66 per cent., the former is tested by the pepsin method as well as qualitatively, to show the nature of the nitrogen source more in detail.

Let me illustrate by giving a few actual figures taken from recent inspections:

Sample No.	Alkaline permanganate availability.		Pepsin availability.
	Organic.	Total.	
A.....	30	43	42
B.....	35	45	45
C.....	39	63	61
D.....	59	59	83
E.....	58	74	83

<sup>1</sup> Vt. Exp. Sta., Rep. 12, 1898, page 139.

The organic nitrogen in samples A and B is certainly open to question. Sample C is somewhat better, while D and E are all that could be desired.

The following tables show the results obtained by the alkaline permanganate and pepsin methods on fifty-one samples of animal and vegetable ammoniates.

Briefly reviewing the results as summarized in Table II, we have in the first group the probably readily available ammoniates. Excepting the three vegetable ammoniates to which the alkaline permanganate method is not applicable, but whose rank is clearly established by the pepsin figure, we find the permanganate availability running from 56 to 68 and the pepsin from 71 to 97 per cent. It should be noted that the pepsin treatment gives a low result, 25 per cent., for hoof meal, against 66 per cent. by the permanganate process. Certain vegetation tests indicate that the higher figure is possibly more nearly correct.<sup>1</sup>

The second group, whether of vegetable or animal origin, shows a decided drop in availability percentage by both methods and fall into the questionable class. The leather preparations were mechanically very fine and dry and in many instances partially soluble in water. Many of them carried a considerable percentage of ammonia, for which credit is given in the column headed "total."

The inert nature of the nitrogen in peat is well recognized. Note the low permanganate availability of 27 per cent. and the pepsin figure of —25 per cent. This negative result indicates that an insoluble nitrogen figure of 125 per cent. was obtained by the pepsin treatment being occasioned by an absorption of nitrogen from the pepsin solution during digestion, which the subsequent washing failed to remove.

Without going into further detail, it seems fair to conclude that the methods are capable of making fairly broad distinctions between ammoniates of presumably high and low nitrogen availability. The former is simple and rapid and very useful as an indicative method, in that it will eliminate quickly such samples as would doubtless rank well by the longer pepsin process or by field and pot experiments.

In addition to the above results, we have previously published data<sup>2</sup> showing the organic nitrogen availability by the alkaline permanganate method on sixty one animal and vegetable ammoniates. Applied to commercial fertilizers, the method has indicated that the organic nitrogen they contained was derived from good sources in a large majority of cases, the range in availability during the past 12 years for company averages being from 34 to 77 per cent.

<sup>1</sup> Conn. (State) Agr. Exp. Sta., Rpts. 18 (1894), pp. 95-100; 19 (1895), p. 112; 20 (1896), pp. 189-190; 21 (1897), p. 270.

<sup>2</sup> Vt. Exp. Sta., Rep. 14, 1900, page 221.

TABLE I.—ALKALINE PERMANGANATE AND PEPSIN AVAILABILITIES.

No.	Material.	Nitrogen content.			Grams, used	Alkaline permanganate availability.		Pepsin availability.
		Total, per cent.	Ammonia, per cent.	Organic, per cent.		Organic, per cent.	Total, per cent.	
1	Dried blood . . . . .	13.79	0.07	13.79	0.33	66	66	93
2	Dried blood . . . . .	14.63	...	14.63	0.31	67	67	97
3	Pig blood . . . . .	13.54	0.68	12.86	0.35	64	66	98
4	Blood flour . . . . .	14.03	...	14.03	0.32	62	62	98
5	Dried fish . . . . .	6.93	...	6.93	0.67	68	68	77
6	Dry mixed fertilizer, Nitrogen from No. 2 . . . . .	4.15	...	4.15	1.08	69	69	95
7	Tankage, high-grade . . . . .	10.23	0.07	10.23	0.44	57	57	79
8	Tankage, high-grade . . . . .	9.78	0.07	9.78	0.46	59	59	77
9	Hog tankage . . . . .	5.63	...	5.63	0.80	52	52	58
10	Bone meal . . . . .	2.66	...	2.66	1.69	56	56	75
11	Cottonseed meal . . . . .	6.40	...	6.40	0.70	46	46	88
12	Castor pomace . . . . .	4.83	0.32	4.51	0.98	46	50	78
13	Ground tobacco stems . . . . .	1.65	...	1.65	2.73	12	12	63
14	Scotch hide and hoof meal . . . . .	14.80	0.14	14.80	0.30	64	64	21
15	Hoof meal . . . . .	15.15	0.28	14.87	0.30	68	69	28
16	Treated leather, foreign . . . . .	8.67	0.07	8.67	0.52	41	41	41
17	Treated leather, foreign . . . . .	8.09	0.07	8.09	0.56	44	44	47
18	Dissolved leather . . . . .	8.25	1.09	7.16	0.63	43	51	47
19	Raw leather . . . . .	8.00	...	8.00	0.56	40	40	53
20	Tyget tankage . . . . .	9.58	0.07	9.58	0.47	52	52	43
21	Solubilized organic nitrogen . . . . .	7.55	0.25	7.30	0.62	48	49	55
22	Solubilized organic nitrogen . . . . .	6.58	0.14	6.44	0.70	45	46	60
23	Original nitrogenous manure . . . . .	7.62	0.41	7.21	0.62	43	46	49
24	Ammoniated manure . . . . .	8.03	1.04	6.99	0.64	43	51	42
25	Nitrogenous manure . . . . .	6.75	0.14	6.61	0.68	46	47	65
26	Nitrogenous manure . . . . .	6.97	0.44	6.53	0.69	49	52	39
27	Extracted leather . . . . .	8.21	...	8.21	0.55	37	37	45
28	Hide and skin . . . . .	7.83	...	7.83	0.58	44	44	44
29	Treated leather . . . . .	7.39	0.10	7.39	0.61	45	45	46
30	Treated leather . . . . .	7.13	0.14	6.99	0.64	46	48	63
31	Muck tankage . . . . .	2.86	...	2.86	1.57	30	30	—12
32	Illinois humus peat . . . . .	2.83	...	2.83	1.59	33	33	—22
33	Nitrogenous material, G. . . . .	3.13	...	3.13	1.44	31	31	—5
34	Kiln-dried peat, Florida . . . . .	2.12	...	2.12	2.12	23	23	—36
35	Air-dried peat, Florida . . . . .	2.07	...	2.07	2.17	23	23	—37
36	Peat, Vermont . . . . .	1.68	...	1.68	2.68	23	23	—25
37	Peat, treated with sulphuric acid . . . . .	0.55	...	0.55	8.18	36	36	19
38	Mora meal . . . . .	2.67	...	2.67	1.69	26	26	46
39	Tartar pomace . . . . .	4.23	0.23	4.00	1.13	22	26	12
40	Tartar pomace . . . . .	3.72	0.28	3.44	1.31	26	31	3
41	Tartar pomace . . . . .	4.54	0.37	4.17	1.08	43	47	29
42	Tartar yeast manure . . . . .	3.74	0.27	3.47	1.30	32	37	6
43	Tartar yeast mixture . . . . .	6.51	0.34	6.17	0.73	39	42	36
44	Tartar yeast mixture . . . . .	4.92	0.25	4.67	0.96	37	41	31
45	Garbage tankage, New York . . . . .	2.10	...	2.10	2.14	21	21	6
46	Garbage tankage, Chicago . . . . .	2.26	...	2.26	1.99	23	23	35
47	Beef refuse compound . . . . .	7.32	2.77	4.55	0.99	15	47	22
48	Ammoniated manure . . . . .	6.18	0.97	5.21	0.86	34	44	23
49	Patent nitrogenous potash manure . . . . .	6.33	1.53	4.80	0.94	15	35	12
50	Fillerine . . . . .	6.28	1.89	4.39	1.03	18	43	14
51	Beet refuse, potash manure . . . . .	4.47	0.14	4.33	1.04	29	31	43

TABLE II.—AVAILABILITY SUMMARY.

Material.	Average alkaline permanganate availability.		Average pepsin availability.
	Organic, per cent.	Total, per cent.	
Dried blood . . . . .	65	65	97
Dried fish . . . . .	68	68	77
Tankage . . . . .	56	56	71
Bone meal . . . . .	56	56	75
Cottonseed meal . . . . .	46	46	88
Castor pomace . . . . .	46	50	78
Tobacco stems . . . . .	12	12	63
Hoof meal . . . . .	66	67	25
Leather preparations . . . . .	44	45	49
Peat . . . . .	27	27	—23
Mora meal . . . . .	26	26	46
Tartar pomace . . . . .	33	37	20
Garbage tankage . . . . .	22	22	20
Sugar beet—gas house refuse . . . . .	21	42	19
Fillerine . . . . .	18	43	14
Beet refuse . . . . .	29	31	43

The latter figure indicates a good grade of material and the former a decidedly poor grade, so much so that steps were taken to see that better materials were used.

The writer recently treated a portion of sample No. 36 with sulphuric acid, allowed the mixture to stand for 3 days on a steam radiator and then neutralized the excess acid with carbonate of lime. The resulting material was dried and ground and is listed in Table I as No. 37. Comparing results, we note that the original peat, which by the way is a composite from 35 samples representing the deposits in Chittenden County, Vermont, shows an availability of 23 by permanganate and —25 by pepsin, while the sulphuric acid-treated residue gave 36 and +19, a gain in availability measured by the permanganate and pepsin methods of 13 and 44 per cent., respectively.

Four of the samples listed in Table I have been recently tested by pot experiments at R. I. Experiment Station. The results as furnished by Dr. Hartwell, together with our results by the permanganate and pepsin methods, are stated below:



Availability by:

Sample No.	Pot experiment.			Alkaline permanganate method.		Pepsin method.
	Barley.	Millet.	Oats.	Organic.	Total.	
23.....	52	70	62	43	46	49
27.....	10	49	38	37	37	45
42.....	19	0	38	32	37	6
49.....	34	39	21	15	35	12

Without discussing the results and variations therein, it is sufficient to observe that both the permanganate and pepsin methods clearly agree as to the superiority of sample 23, and are in accord with the results by pot experiment.

The writer has found it useful in interpreting availability figures secured by laboratory methods to determine the ratio between organic nitrogen and the organic matter present, in both crude stock and fertilizers.

The testing of crude nitrogenous stock by field or pot experiments will, of course, show their availability when used alone or in dry mixed goods. Another factor is introduced when these materials are used in so termed wet mixed goods. The organic nitrogen is here subjected to a sulphuric acid treatment and considerable heat is produced which, judging from analogy with the results by the Kjeldahl nitrogen process, cannot decrease the availability.

It is impossible to duplicate the manufacturing process on a small scale in the laboratory, although the use of a fireless cooker after the addition of sulphuric acid has been suggested. To settle this interesting point it will be necessary for the manufacturer to work with parties who are so situated that they can conduct availability experiments, at least to the extent of furnishing suitable quantities of authentic samples of the various questionable nitrogen-containing materials, before and after the sulphuric acid treatment.

The writer clearly realizes that both the methods outlined are empirical and far from perfect, but believes it nevertheless true that by their use the majority of goods of unquestionable excellence as to nitrogen availability may be quickly and positively eliminated, leaving a relatively small number for more elaborate examination.

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## THE DETECTION OF INFERIOR AMMONIATES IN COMMERCIAL FERTILIZERS.

By JOHN PHILLIPS STREET.  
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It is a recognized fact that the use of a filler in commercial fertilizers is often necessary and at times even desirable if a dry and friable fertilizer is to be obtained that will not clog on drilling. When a filler is used for this purpose alone there is no legitimate objection to its use, provided that the claimed com-

position of the fertilizer is maintained and provided that the use of fillers does not encourage to too great a degree the manufacture of low-grade mixed fertilizers, which are always a relatively expensive form of plant food for the farmer.

In recent years, however, the subject of fillers has taken a different aspect. It has been found that dried peat is an admirable absorbent and that its use in a fertilizer generally assures excellent mechanical condition. Fortunately, or unfortunately, dried peat contains a considerable percentage of nitrogen, often over 3 per cent., which repeated experiments have shown to be exceedingly inert. The use of such a nitrogen-bearing filler in compounding mixed fertilizers has given the agricultural chemist much difficulty in interpreting his results, especially when by the policy of the fertilizer control of his state he is expected to affix a commercial valuation to the mixture. No one will argue that dried peat should receive the same valuation as blood, high-grade tankage, fish, bone or cottonseed-meal. Accordingly, it is incumbent upon the chemist to devise some method whereby this inferior form may be differentiated from those whose value is unquestioned. The manufacturers claim that the amount of peat used seldom exceeds 200 or 300 lbs. per ton. In a high-grade fertilizer, guaranteeing 4 or 5 per cent. of ammonia, it is admitted that the introduction of this relatively small amount of peat is without great practical significance. But in the case of the numerous class of fertilizers, carrying a guaranty of 1 per cent. ammonia, the problem is quite different, for here the peat nitrogen may easily make up one-half of the total nitrogen, a condition which I found in at least one brand during my last inspection.

Various methods have been suggested for the detection of peat in mixtures, the microscope, the various permanganate or potash methods and the pentosan method of the writer. In a dry-mixed fertilizer the microscope is of undoubted value in the detection of peat, but where the wet-mixing process has been employed it is far more reliable. The alkaline permanganate method of Jones has given excellent results in the hands of some chemists, but personally I have never been able to control conditions so as to warrant uniform determinations made at different times with this method. The neutral permanganate method suggested by the writer some years ago has given excellent results with raw materials, clearly distinguishing between high-grade and inferior ammoniates. When applied to mixed fertilizers, however, the details of manipulation hitherto given with the method fail to furnish any sharp line of demarcation between the good and the bad. The pentosan method, likewise suggested by myself, is too local in its application to be of much practical value. In states like my own, Connecticut, where immense

quantities of cottonseed meal are used either alone or in mixtures, the pentosan method is practically valueless.

Convinced that the neutral permanganate method was based on proper principles, I have been working recently to determine whether certain modifications might not be introduced which would render it a reliable, workable method.

During our last inspection of fertilizers in Connecticut, it was observed that the filtrate in the citrate-insoluble phosphoric acid determination was often very dark colored, sometimes almost opaque, ranging from a reddish brown to nearly black. This appearance suggested the presence of a humus-bearing material, and the number of all samples yielding these dark-colored filtrates were noted and later tested by the neutral permanganate method.

The method used was as follows: Weigh on to a moistened 9 cm. S. & S. No. 595 filter a quantity of the fertilizer equivalent to approximately 45 mgs. of organic nitrogen and wash with water at room temperature to about 200 cc. Transfer filter and contents to a 300 cc. low-form Griffin beaker, and digest with 125 cc. of 1.6 per cent., neutral potassium permanganate solution in a hot water bath for thirty minutes. Set the beaker down in the bath so that the surrounding water shall be higher than the solution in the beaker, cover with a watch-glass, and stir twice at intervals of ten minutes with a glass rod. At the end of the digestion remove from bath, add 100 cc. of cold water, and filter through a heavy folded filter. Wash with cold water, small quantities at a time, until the total filtrate amounts to 400 cc. When sufficiently dry to handle, transfer filter and contents to a nitrogen flask and determine nitrogen by the Kjeldahl method. The nitrogen obtained, less the blanks from the two filters used, is the nitrogen not oxidized by the permanganate.

The only essential difference between this and the method earlier suggested by me, is the amount of material taken, a change of great importance, as will be shown later.

As a preliminary test of the method, eight mixtures were prepared. These were all made in 50-gram portions, each containing 10 grams of muriate of potash and varying amounts of organic nitrogenous material, each yielding, with the exception of No. 8, 1.50 per cent. of nitrogen in the total mixture; acid phosphate was then added to each mixture to make up a total of 50 grams. The exact proportions of the ingredients follow, omitting the muriate of potash, which was 10 grams in each:

No. 1	5 grams dried blood.	34.5 grams acid phosphate.
No. 2	10 grams tankage.	29.5 grams acid phosphate.
No. 3	30.0 grams garbage tankage.	10.0 grams acid phosphate.
No. 4	11.0 grams cottonseed-meal.	29.0 grams acid phosphate.
No. 5	8.5 grams fish.	31.5 grams acid phosphate.
No. 6	20.0 grams ground bone.	20.0 grams acid phosphate.
No. 7	25.0 grams peat.	15.0 grams acid phosphate.
No. 8	8.0 grams peat, 8 g. blood.	27.0 grams acid phosphate.

The following tabulation shows the availability figures obtained in the original raw materials and in the same materials after they were mixed with acid phosphate and muriate of potash:

	Availability.	
	In original material.	In mixed fertilizer.
Dried blood.....	95.6	92.9
Tankage.....	95.1	91.8
Garbage tankage.....	58.9	75.1
Cottonseed-meal.....	95.1	92.9
Dried fish.....	96.4	90.0
Ground bone.....	93.6	92.0
Peat.....	47.8	37.1
Dried blood and peat.....	89.1	86.0

It will be observed that the method shows blood, tankage, cottonseed-meal, fish and bone to possess a higher degree of availability either as determined in the original material or when mixed with acid phosphate and muriate of potash. On the other hand, garbage tankage shows a much lower availability, while peat shows about one-third the availability of any of the high-grade ammoniates. The differentiation is most marked, and I would have no hesitation in classing as doubtful a fertilizer showing less than 90 per cent. availability by this method, an inferior one showing less than 80 per cent.; one showing less than 50 per cent. must be classed as made from very inferior ammoniates.

The mixture of peat and blood was interesting. By error I introduced more blood in the mixture than I intended, and the peat nitrogen only made up one-seventh of the total nitrogen; but even this small amount of peat was sufficient to reduce the availability from 92.9 to 86 per cent., thus placing it in what I should call the doubtful class.

Let us now consider the practical application of this method. Seventeen samples of mixed fertilizers aroused our suspicion by the dark-colored citrate filtrates already referred to. These were all tested by the neutral permanganate method, using 2 grams material and 75 and 45 mg. of organic nitrogen respectively. The results are tabulated below:

		Availability of organic nitrogen			
		2 grams	75 mg.	45 mg.	
No.	Total N.	Organic N.	materials.	org. nit.	
9.....	4.72	3.51	80.2	81.6	93.3
10.....	5.16	2.62	84.7	81.2	88.9
11.....	3.59	2.48	84.1	80.5	85.3
12.....	4.28	2.08	90.0	84.7	89.3
13.....	2.34	2.04	80.0	69.5	78.5
14.....	2.72	1.84	83.2	74.2	85.4
15.....	3.06	1.62	84.7	67.3	83.2
15a.....	.....	1.10	.....	57.0	70.9
15b.....	.....	2.20	.....	75.6	89.7
16.....	2.72	1.62	78.7	69.5	77.3
17.....	2.14	1.60	81.9	71.7	76.4
18.....	2.20	1.56	79.8	70.1	74.6
19.....	2.95	1.48	83.1	69.1	77.1
20.....	1.63	1.47	79.9	70.5	76.9
21.....	2.27	1.41	78.0	64.0	75.1
22.....	2.88	1.26	77.8	75.2	74.0
23.....	1.14	1.02	76.0	61.5	67.8
24.....	1.10	0.86	67.4	58.7	62.4
25.....	0.95	0.50	75.0	54.3	62.8
25a.....	.....	0.54	.....	46.4	54.7
25b.....	.....	0.43	.....	63.7	70.9

The results where 2 grams of material were used show insufficient differences in availability to make results conclusive. The range was from 67.4 to 90.0, with an average of 80.3.

Where 75 mg. of organic nitrogen were used striking differences were obtained, but, owing to the large amounts of material used, the permanganate was in excess (as shown by the colored filtrate) in only 4 out of 21 cases, thereby introducing a possible inaccuracy in the results. The range was from 54.3 to 84.7, with an average of 80.7.

Where 45 mg. of organic nitrogen were used the results are very satisfactory, only 2 of the 21 samples not showing the permanganate color in the filtrate. The range was from 62.4 to 93.3, with an average of 78.1. Fortunately we know something of the history of certain of the samples which aids us materially in judging the value of the method. In every case where the presence of peat was suspected from the color of the citrate filtrate, the manufacturer was advised of our finding. In some cases the use of peat was frankly admitted, together with the amount used per box, in others the use of peat denied and a satisfactory explanation made. For instance, in Nos. 9 and 10 the manufacturer denied the use of peat but admitted the use of 150 lbs. of dirt per box; our availability figures of 93.3 and 88.9, respectively, confirm the correctness of his statement and show that the color of the citrate filtrate, unsupported by other evidence, is not conclusive as to the presence of peat. In No. 17 the manufacturer admits using 246-2.67 per cent. nitrogen; the availability figure is 76.4.

In No. 15 the manufacturer admitted that he had used 312 lbs. of peat (2.7 per cent. nitrogen) per ton in one of the samples making up our composite, while in the other no peat, but high-grade blood, was used.

The separate samples, Nos. 15a and 15b, in the table, were tested, and in one an availability of 70.9 was obtained and in the other 89.7, thus confirming the manufacturer's statement and proving the value of the method. In No. 25, from the same manufacturer, a similar statement was made, 25a containing 200 lbs. peat (2.5 per cent. nitrogen) and 25b no peat (the form of nitrogenous material used was not stated). In the peat portion the availability was 54.7, in the other 70.9; apparently in the latter some other relatively inert form of nitrogen was used, assuming the manufacturer's statement to be correct.

By this method, setting the minimum availability at 80, 13 of these samples would be condemned and 6 passed, the last without exception being fertilizers in which the total nitrogen is high, and the water-soluble nitrogen also relatively high. Three of these we know to contain no peat.

Twenty samples of tankage and three of garbage

tankage were also tested by this method. The availability of 18 samples of tankage ranged from 87.9 to 94.0, with an average of 92.5; the other 2 tankages showed availabilities of 81.6 and 83.7, which, together with their low percentage of phosphoric acid, suggested the presence of peat. The three garbage tankages showed availabilities of 47.5, 48.0 and 51.1.

#### AVAILABILITY OF SOIL NITROGEN IN RELATION TO THE BASICITY OF THE SOIL AND TO THE GROWTH OF LEGUMES.

BY T. LYON AND J. BIZZELL, U. M. A. BULL.

Received April 11, 1914.

It is well known that the lack of lime compounds in the soil is a serious hindrance to the growth of alfalfa. The application of lime to the soil not only produces a larger growth but also a better color of the alfalfa plants. These differences may frequently be noticed to extend to the grass or to the weeds growing with the alfalfa. The beneficial effects of the lime are apparently shared by the vegetation associated with the legume.

The question as to the nature of the processes by which this improvement takes place naturally presents itself. The phenomena observed on our experiment plats were these: (1) The alfalfa grew better and had a better color on the limed soil. (2) The grass and weeds growing with the alfalfa were likewise better on the limed soil. (3) On two plats of land both of which were limed, but one of which was planted to timothy and the other to a mixture of alfalfa and timothy, the timothy made a better growth on the plat having the mixture.

Analyses were made of alfalfa from ten plats of land. One-half of each plat had been limed four years before at the rate of 3,000 pounds of quicklime per acre. The indicated lime requirement of the top foot of soil as determined by Veitch's method was 4,000 pounds per acre. In every case the alfalfa from the limed portion of the plats contained a higher per cent. of nitrogen. All samples of alfalfa were taken at the same time, and represented as closely as possible the same stage of growth. Examination of the alfalfa roots showed the presence of tubercles in practically all cases. The difference in composition was, therefore, not due to the presence or absence of tubercles, which has been shown by Smith and Robinson<sup>1</sup> to influence the nitrogen content of alfalfa.

On these plats *Erigeron annuus* was a common weed, and this apparently shared the good or poor condition of the alfalfa. Samples of the weed were taken from the limed and unlimed portions of each plat. Nine of the ten plats produced plants with a higher nitrogen content on the limed soil.



The following table shows the close relation between the basicity of the soil, the yield of alfalfa, and the nitrogen content of the alfalfa and of the weed *Erigeron annuus* growing with it:

TABLE I.—EFFECT OF LIMING SOIL ON THE COMPOSITION OF ALFALFA, *ERIGERON ANNUUS*, GROWING WITH IT AND ALSO ON THE NITRATES IN THE SOIL.

Plat No.	Treatment.	Yield of hay first cutting.	Per cent alfalfa in mixed hay.	Per cent. nitrogen		
				in pure alfalfa (water-free).	in <i>Erigeron annuus</i> (water-free).	in dry soil, p.p.m.
741	Limed.....	103	50	2.65	1.17	2.6
	Unlimed.....	49	30	2.23	1.52	3.8
742	Limed.....	131	80	3.36	1.67	9.7
	Unlimed.....	110	75	2.74	1.26	5.6
743	Limed.....	138	70	3.53	1.76	7.1
	Unlimed.....	96	65	3.04	1.43	4.3
744	Limed.....	122	55	3.13	1.74	7.8
	Unlimed.....	107	60	2.52	1.38	5.4
745	Limed.....	130	80	3.55	1.96	20.4
	Unlimed.....	86	70	2.57	1.46	2.9
746	Limed.....	112	80	3.46	1.94	3.3
	Unlimed.....	96	80	2.99	1.34	1.7
747	Limed.....	103	80	3.39	1.63	3.6
	Unlimed.....	69	70	2.24	1.38	2.9
748	Limed.....	88	88	3.21	1.79	8.6
	Unlimed.....	79	75	2.38	1.41	7.7
749	Limed.....	69	70	3.54	1.74	9.8
	Unlimed.....	47	70	2.35	1.42	5.1
750	Limed.....	85	60	3.19	1.68	8.7
	Unlimed.....	15	20	2.38	1.47	3.3

It is very apparent from these figures that the nitrogen content of alfalfa is increased by the addition of lime to the soil. In the case of the accompanying non-leguminous vegetation there still remained a question as to whether the higher percentage of nitrogen is due to the effect of lime or to some influence either direct or indirect that could be traced to the better stand and growth of alfalfa on the limed soil.

To throw some light on this question, samples of timothy hay were analyzed. Samples I and II were grown on land that was limed. Sample I was grown on a plat of alfalfa and timothy mixed. Sample II had no alfalfa sown with it. Both analyzed samples were pure timothy. Similar determinations were made of timothy grown on unlimed land of which Sample III was grown with alfalfa and Sample IV without alfalfa:

TABLE II.—NITROGEN CONTENT OF TIMOTHY GROWN WITH AND WITHOUT ALFALFA.

Soil treatment.		Crop treatment.		Per cent. nitrogen in timothy water-free.
Sample I.	Limed	Grown with alfalfa		2.49
Sample II.	Limed	Grown without alfalfa		2.04
Sample III.	No lime	Grown with alfalfa		1.55
Sample IV.	No lime	Grown without alfalfa		1.44

Samples I and II cannot be compared with samples III and IV as I and II were taken June 1st, and III and IV on June 19th, the percentage of nitrogen naturally being greater in the younger grass. It may be concluded from these results that the growth of alfalfa

influences the nitrogen content of the timothy growing with it, whether growing on limed or unlimed soil. It does not, however, permit of any conclusion as to the effect of lime alone on the composition of the timothy.

Table I contains a statement of the nitrates present in the soil at the time the alfalfa was harvested. It will be noticed that on every plat except Plat 741 the nitrates were higher on the limed than on the unlimed soil, in spite of the fact that the yields of hay were much greater on the limed soils. As the crop was a legume, it cannot be positively stated that the draft of the crop upon the nitrates in the soil was greater on the limed soil. It, nevertheless, raises the question whether nitrification is favored by the addition of lime to the soil when the soil is in need of lime. In other words, whether an increase in the basicity of the soil makes it more favorable for nitrification. Another question raised is whether the more luxuriant growth of the alfalfa on the limed soil produced a condition more favorable to nitrification.

As a means of gaining information on this subject, nitrification tests were made in soils from a series of plats, of which four had been limed at the rate of 2,000 pounds per acre four years before, and four had never received any lime. Two of these plats were planted to alfalfa, both on the limed and unlimed portions, one to a mixture of alfalfa and timothy limed and unlimed, and one to timothy alone limed and unlimed.

The nitrification tests were made according to the following method: 100 grams of the moist soil were placed in a 250 cc. bottle. To this was added 500 milligrams of ammonium sulfate and sufficient water to bring the soil to a moisture content of 25 per cent. calculated on the basis of dry soil. The bottle, after insertion of a tight cotton plug in the mouth, was placed in the incubator and kept at a temperature of 30° C. for ten days in the case of one test and twenty days in the other.

TABLE III.—NITRIFICATION TESTS IN SOILS LIMED AND UNLIMED AND WITH AND WITHOUT ALFALFA.

Plat No.	Treatment.	Crop.	Nitrates		
			Nitrates at end of 10 days in original soil.	Nitrates at end of 20 days test day.	Nitrates at end of 20 days test day.
			p.p.m. dry soil.	p.p.m. dry soil.	p.p.m. dry soil.
4001a	Limed	Alfalfa	5.5	182	381
4002a	Limed	Timothy	7.4	152	361
4003a	Limed	Alfalfa and timothy	8.0	202	384
4004a	Limed	Alfalfa	10.5	196	402
Average for limed plats.			7.8	208	382
4001c	Not limed	Alfalfa	8.0	100	148
4002c	Not limed	Timothy	6.2	83	148
4003c	Not limed	Alfalfa and timothy	8.5	86	167
4004c	Not limed	Alfalfa	5.5	61	110
Average for unlimed plats.			6.9	77	128

Apparently there was a much more active nitrification due to the incorporation of lime with the soil.

This holds good not only for the averages of the limed and unlimed soils but also for each one of the plats so treated.

The limed plats containing alfalfa have in each case produced more nitrates than the limed soil growing no alfalfa, but where no lime was added the presence of alfalfa does not seem to have had any effect on nitrification.

It may be concluded from these experiments that a substantial increase in the basicity of a soil favors nitrification, and that the growth of alfalfa, and possibly other legumes, on soil well supplied with lime, also contributes to the nitrifying process. Whether the alfalfa acts in this way by increasing the quantity of easily decomposing organic matter through the production and decomposition of tubercles, or small roots, or in some other way, has not been demonstrated.

#### CONCLUSIONS.

These experiments confirm the opinion heretofore held that the presence of a certain degree of basicity in the soil is favorable to nitrification, and that the addition of lime produces a substantial increase in the nitrates for at least four years after its application.

Soil on which alfalfa grew possessed greater nitrifying power than did similar soil cropped to timothy. The growth of a legume is thus apparently favorable to the process of nitrification.

Alfalfa grown on soil in need of lime contained a higher percentage of nitrogen when lime was added to the soil than when none was added. The average difference on ten limed and ten unlimed plats amounted to 88 pounds of crude protein per ton of alfalfa hay containing 10 per cent. moisture.

Timothy growing with alfalfa contained a higher percentage of nitrogen than did the same grass growing alone. When the crop was produced on land that had been well limed this difference was more marked. A possible improvement in the nitrogen content of certain plants by growing them with legumes is thus indicated.

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### THE EFFECT OF LIME UPON THE SOLUBILITY OF SOIL CONSTITUENTS.

By E. W. GAITHER.

Received May 11, 1910.

In the review of literature upon the subject of the effect of lime upon the solubility of soil constituents, the writer finds that most of the work done has been done with water extracts, and it seems that no definite conclusions can be drawn from the little that has been accomplished.

Work done of Whitson and Stoddard<sup>1</sup> shows that

acid soils are deficient in phosphorus, soluble in N/5 HNO<sub>3</sub>, or in calcium phosphate, and unpublished work done in this laboratory shows that soils low in lime soluble in N/5 HNO<sub>3</sub> are also low in phosphorus in the same solution.

Morse and Curry<sup>1</sup> have shown that lime treatment of soils, for comparatively short periods, does not increase the solubility of potassium, and decreases that of aluminium and iron in water extracts.

Frapps,<sup>2</sup> and Whitson and Stoddard<sup>3</sup> have shown that the N/5 HNO<sub>3</sub> method is reliable for measuring calcium phosphate in soils, but so far as the writer knows, there has been no attempt to determine the effect of lime upon the solubility of other elements present in the soils soluble in N/5 HNO<sub>3</sub>, or other weak acid solutions.

Crop experiments at the Rhode Island Station<sup>4</sup> have indicated that there is no appreciable effect upon the availability of potash by the lime treatment.

The fact that calcium phosphate, whether added or originally in the soil, becomes available to plants, seems to be fairly well established by data obtained by N/5 HNO<sub>3</sub> digestion of soils, crop production of these soils, and crop production by the use of floats and slag.

These facts, together with the statement that the addition of lime and roasted phosphates of iron and aluminum, or other forms of phosphorus, to the soil increases the available phosphorus in these phosphates,<sup>5</sup> would point to the conclusion that the N/5 HNO<sub>3</sub> digestion of the limed soil would give an increased amount of phosphorus in this solution.

Furthermore, if lime replaces iron and aluminum in combination with phosphorus, and the iron and aluminum are precipitated in the soil, we would expect to find an increased amount of these elements in the acid solution.

Following this line of deduction, we would expect the silicates to be broken up and to follow the same course—not only the silicates of iron and aluminum, but those of Mg and K to a greater or less extent. If this were true, we would naturally expect to find an increase in the amount of potassium and magnesium soluble in N/5 HNO<sub>3</sub>.

Unpublished results obtained at this station, in connection with soil fertility experiments, by the analysis of wheat grown on plots with various forms of fertilization and one end limed in 1900, the other in 1905, with 1 ton CaO per acre, seem to give good grounds for the conclusion that the addition of lime to these soils decreases the potassium that may be assimilated by the crop, while, as indicated by the

<sup>1</sup> 19th and 20 Report N. H. Agr. Expt. Sta., pp. 310-292.

<sup>2</sup> Jour. Amer. Chem. Soc., 28, 824.

<sup>3</sup> Research Bull. No. 2, U. of Wis. Agr. Expt. Sta., p. 60.

<sup>4</sup> R. I. Expt. Sta. Bull. 139, p. 75 and appended references.

<sup>5</sup> R. I. Expt. Sta. Bull. 139, p. 72, and appended references. THIS JOURNAL, 2, 133-135.

<sup>1</sup> Research Bull. No. 2, U. of Wis. Agr. Expt. Sta., p. 60.

analysis of the same crop, we find an increased per cent. of phosphorus in the crop where lime was used in 1905 over the crop where lime was used in 1900, as is shown by Table I:

TABLE I.—EXTRACTS FROM RESULTS OF ANALYSES OF WHEAT GROWN ON LIMED AND UNLIMED PLOTS.

		Per cent. $K_2O$ .	Per cent. $P_2O_5$ .
No fertilizer, limed 1900	1 ton CaO per acre	0.770	0.305
No fertilizer, limed 1905	1 ton CaO per acre	0.729	0.368
Phosphorus, limed 1900	1 ton CaO per acre	0.724	0.340
Phosphorus, limed 1905	1 ton CaO per acre	0.612	0.413
Phosphorus and potash, limed, 1900	1 ton CaO per acre	0.835	0.351
Phosphorus and potash, limed 1905	1 ton CaO per acre	0.816	0.402
Potash, limed 1900	1 ton CaO per acre	0.885	0.327
Potash, limed 1905	1 ton CaO per acre	0.801	0.352

These facts led to an effort to show, in a chemical way, the effect of lime upon the soil constituents, and after making some determinations of water-soluble constituents, before and after various treatments with lime, without much light being thrown upon the subject, the writer concluded to try the N/5

phosphate, after separating with bromine and the  $Fe_2O_3$  and  $Al_2O_3$ , which were dissolved from the filter after the double acetate precipitation, and separated by a 50 per cent. solution of KOH. The  $Al_2O_3$  was then precipitated as  $AlPO_4$ . A separated portion was pipetted off for  $Fe_2O_3$  and precipitated with  $NH_4OH$ . After washing, the precipitate was dissolved with HCl and reduced with stannous chloride and titrated with  $N/200 K_2Cr_2O_7$ , using  $HgCl_2$  to precipitate the excess of stannous chloride. The filtrates were tested for iron and found free. The results are shown in Table II.

It is interesting to note the uniform increase in the solubility of all the substances determined, with the single exception of  $K_2O$ , which does not vary materially for any application of lime, except where 2 tons per acre were used, which does not indicate that the amount of lime added causes this increase.

It seems that these results show that the phosphates and silicates are in a measure broken up by lime with the exception of the silicates carrying

TABLE II.

No. CaO per acre.	$P_2O_5$	MgO.	$Al_2O_3$ .	$Fe_2O_3$ .	$SiO_2$ .	$Mn_2O_4$ .	CaO.	$K_2O$ .
Check.....	0.00216	0.0321	0.0982	0.0375	0.0245	0.0295	0.0899	0.0089
Check.....	0.00252	0.0376	0.0989	0.0364	0.0290	0.0281	0.1031	0.0104
No. 4000.....	0.00225	0.0342	0.1006	0.0440	0.0545	0.0335	0.2953	0.0133
No. 8000.....	0.00284	0.0321	0.1206	0.0552	0.0800	0.0405	0.5239	0.0089
No. 12000.....	0.00428	0.0326	0.1316	0.0656	0.1000	0.0443	0.7771	0.0093
No. 16000.....	0.00486	0.0360	0.1480	0.0704	0.1215	0.0456	0.8926	0.0087
No. 20000.....	0.00720	0.0488	0.2000	0.0880	0.1730	0.0706	1.2738	0.0084
No. 24000.....	0.00796	0.0512	0.1956	0.0952	0.1970	0.0741	1.4260	0.0087
No. 30000.....	0.00860	0.0560	0.2327	0.1104	0.2230	0.0867	1.5774	0.0096
No. 36000.....	0.00999	0.0618	0.2399	0.1424	0.2740	0.1071	2.0724	0.0100
No. 40000.....	0.01094	0.0664	0.2431	0.1568	0.2925	0.1108	2.3034	0.0090
No. 50000.....	0.01300	0.1064	0.2853	0.1824	0.3150	0.1296	2.6664	0.0080

NOTE.—Samples 1 and 2 explanation: Sample 1 was taken when the soil was put into the pots, air-dried and prepared, sealed in tight jar. Sample 2 was taken from the check pot receiving no lime but crop grown on this the same as on the other pots. All other samples received lime as indicated in column 1, the lime being mixed with the soil in proportion to weight, assuming 2,000,000 lbs. to be weight of an 8" acre.

$HNO_3$  method on some soil that was being used to test the effect of caustic lime upon the growth of alfalfa, five-gallon earthenware pots being used.

The soil was taken from a portion of the Station farm not under systematic cultivation, and classed by the U. S. Bureau of Soils as Volusia Silt Loam, lime being added as shown in the following table.

The samples were taken a few weeks before the second crop of alfalfa, grown in the pots, was harvested. The samples were air-dried and passed through a  $1/2$  mm. sieve, 10-gram portions being used for preliminary digestion to determine the amount of  $HNO_3$  required to make the solution N/5 at the end of the digestion. Two hundred and twenty grams were then weighed into 2500 cc. Winchester bottles and 2200 cc. of  $HNO_3$  solution added, which would give a solution N/5 at the end of the digestion. This was shaken at intervals of 30 minutes for 5 hours and filtered. The portions for analysis were pipetted off in duplicate as follows: For  $P_2O_5$ , 400 cc.; for  $SiO_2$ ,  $Mn_2O_4$ , CaO, MgO and  $K_2O$ , and  $Al_2O_3$ , 400 cc. Determinations were made by the official methods, except  $Mn_2O_4$ , which was determined as the

potassium, which, if attacked at all, are not disturbed sufficiently to liberate the potash to an appreciable extent.

#### CONCLUSIONS.

Lime renders insoluble phosphates in the soil soluble, by replacing iron and aluminum, which is in combination with the phosphorus and renders all three more soluble in N/5  $HNO_3$ .

Lime breaks up certain silicates in soils and renders them more soluble in N/5  $HNO_3$ , but does not act upon insoluble potassium compounds in the soil to such an extent that N/5  $HNO_3$  can be used as a measure of such potassium.

The addition of caustic lime to soils has the effect of diminishing the amount of  $K_2O$  assimilated by wheat grown on such soils.

The theory held, "that lime added to the soil increases the amount of available potash in the soil," is either erroneous, or requires more positive proof than has heretofore been obtained before it can be accepted.



## THE DETERMINATION OF HUMUS.

By F. J. ALWAY, E. K. FILES, AND R. M. PINCKNEY.

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The term *humus* is used in this country with two distinct meanings, the one including the whole of the more or less altered organic matter in the soil and the other only that portion of the black or brown material soluble in dilute alkalis. In the present article, the term is used to signify only the part of the organic matter dissolved by ammonia after lime and magnesia have been previously removed by treatment with dilute hydrochloric acid. The results obtained by treating the same soil with 4 per cent. ammonia solution differ from 10 to 230 per cent., according to whether the Hilgard method or that of the Association of Official Agricultural Chemists, which is commonly spoken of as the "official" method, be employed. The most important work on humus has been done by Hilgard, but his data cannot be compared with those obtained by the A. O. A. C. method. While but a comparatively small amount of data based upon the use of the latter has been published, it is still commonly accepted both in America and in England<sup>1</sup> as a reliable method and is the one in common use.

Humus as defined above is the *matière noire* of Grandeau and the different methods which have been proposed for its determination are modifications of his original method.<sup>2</sup>

Hilgard,<sup>3</sup> to prevent puddling of the soil, placed it in a filter of paper and then covered it with a disc of filter paper, before the preliminary treatment with dilute hydrochloric acid and distilled water. The soil was then treated with 4 per cent. ammonia water until the filtrate came through colorless.

Huston and McBride<sup>4</sup> made a critical study of the Grandeau method as used by Hilgard and as a result recommended the method, which soon after, with a few minor modifications, was adopted by the Association of Official Agricultural Chemists. They determined the humus in eight different soils, four of which were of a peaty nature, both by the Hilgard (called by them the Grandeau) method and by their own. They found the results obtained by the latter to be from 20 to 117 per cent. higher than those obtained by the former. Assuming that this increase was due to the more complete extraction of humus by their method, they regarded the method of Hilgard as unreliable. What they had, in fact, done was to incorporate a large amount of clay with the humus. Upon ignition, after drying, this clay lost water, thus increasing the total loss in weight on ignition, which they, like Grandeau and Hilgard, considered to represent the humus. Both the latter,

however, obtained ammoniacal filtrates practically free of clay, this being retained by the soil through which the ammonia had to pass. To the entire failure of Huston and McBride to take cognizance of the greatly increased amount of so-called "humus ash" obtained by their method is due their erroneous conclusions as to the reliability of the Hilgard method.

About the same time Snyder<sup>1</sup> published the description of a modification of the Grandeau method, in many respects similar to that of Huston and McBride. Frear,<sup>2</sup> in 1901, pointed out the source of error in the official method and suggested a modification of it. Cameron and Breazeale,<sup>3</sup> two years later, determined the humus in six soils, using both the official method and the modification suggested by Frear, *viz.*, the use of a Pasteur-Chamberland filter. They obtained only from one-half to one-twentieth as much humus by the latter as by the former method. They called attention to the fact that it was not certain that some of the humus had not been absorbed and thus removed from the solution and that "humus determinations are tedious, especially if recourse must be had to the filter."

Peter and Averitt,<sup>4</sup> referring to the unreliability of the official method, suggested that the results so obtained be corrected by deducting one-tenth of the weight of the so-called "humus ash."

Moors and Hampton<sup>5</sup> introduced another modification of the Huston-McBride method intended to remove the suspended mineral matter. Using five soils, they compared the results obtained by their method with those obtained, by the official method, by the Cameron and Breazeale modification, and with the Peter and Averitt corrected results. They concluded that while the official method gave results far too high, the Cameron-Breazeale method gave results from 33 to 100 per cent. too low, and that a correction of 14 per cent. gave more nearly correct results than that of 10 per cent.

Notwithstanding the above criticisms of the Huston and McBride method which have appeared, it is still retained as the method of the Association of Official Agricultural Chemists.<sup>6</sup>

*Description of Soils.*—In the soils used, we had representatives of the arid IX, XII and XIII, of the semi-arid III, IV, V, VI, VIII and XI, and of the distinctly humid soils, VII and X. The other samples belong to the eastern portion of the transition region of the Great Plains.

No. I. A composite of surface six-inch samples from a field of upland loess near the Nebraska Experiment Station farm. The field had been in cultivation for about forty years, with heavy applica-

<sup>1</sup> Hall: *The Soil*, 2nd Edition, p. 165 (1908).<sup>2</sup> *Traité d'Analyse des Matières agricoles*, 3rd Edition, I, p. 150 (1897).<sup>3</sup> *Bull. 35*, Bur. of Chem., U. S. Dept. of Agri., p. 80 (1893).<sup>4</sup> *Bull. 35*, Bur. of Chem., p. 84 (1893).<sup>1</sup> *J. A. C. S.*, 16, 210 (1894).<sup>2</sup> *Bull. 69*, Bur. of Chem., p. 40 (1902).<sup>3</sup> *J. A. C. S.*, 26, 29 (1904).<sup>4</sup> *Kentucky Bull.*, 126, 63 (1906).<sup>5</sup> *J. A. C. S.*, 30, 805 (1908).<sup>6</sup> *Bull. 107* (Revised), Bur. of Chem., p. 19 (1908).

tions of barnyard manure during the last twelve. Normal annual precipitation = 29.36 ins.

No. II. A composite of surface six-inch samples from a virgin prairie near Broken Bow, Nebr. The soil is loess though more sandy than No. I. Normal annual precipitation = 25.35 ins.

No. III. The surface four inches of soil from a virgin prairie near Madrid, in western Nebraska. A sandy loam residual soil. Normal annual precipitation is about 18 ins.

No. IV. A composite of many samples taken to a depth of twelve inches from both cultivated and prairie fields near Moose Jaw, Sask., Canada. The soil is a heavy lacustral clay derived from the drift material and deposited in glacial Lake Saskatchewan. Normal annual precipitation is about 15.6 ins.

No. V. The surface foot from the virgin prairie near Lethbridge, Alberta, Canada. A clay loam, probably similar in origin to No. IV. Normal annual precipitation is about 14 ins.

No. VI. Surface six inches from virgin prairie near Solano, northeastern New Mexico. A loam of residual origin. Altitude 6000 feet. Normal annual precipitation is about 16 ins.

No. VII. Surface soil from near Cloudercroft in the Sacramento Mountains, New Mexico. A black loam. A dense growth of coniferous trees covers the mountains at the altitude where the sample was secured, viz., 8,000 feet. Normal annual precipitation = 25.14 ins.

No. VIII. Surface foot of soil from Parsons' dry land orchard near Parker, Colorado. Normal annual precipitation is about 17 ins.

No. IX. Surface six ins. from recently broken grass land in Sulphur Spring Valley, Arizona, eighteen miles north of Douglas, which lies on the Mexican boundary. Soil of alluvial origin. Normal annual precipitation = 10.5 ins.

a residual soil derived from basalt. Normal annual precipitation = 14.2 ins.

No. XII. Surface six inches from long cultivated field east of Fresno, California. A red loam which had never been irrigated. Normal annual precipitation = 9.00 ins.

No. XIII. Surface six inches of sandy alluvium near Delano, California. The field had been under "dry-farming" about 20 years, being non-irrigable. Normal annual precipitation = 6.07 ins.

1433. From the same prairie as III.

902 to 917. Similar to I, but taken to a depth of 12 inches.

*Comparison of Results Obtained by Different Methods.*—With all the methods the soils were treated similarly previous to the application of ammonia, the lime and magnesia being washed out with 1 per cent. hydrochloric acid and the acid removed by washing with distilled water. It was found economical of time, as most of the soils were of fine texture, to use an ordinary filter in a funnel without suction, rather than a Gooch crucible with an asbestos filter. In all determinations a 4 per cent. solution of ammonia was used. Freshly distilled ammonia was used because an ammonia solution allowed to stand in bottles of ordinary glass soon dissolves enough to seriously affect the amount of residue remaining after the ignition—the so-called humus ash. The humus extract, by whichever method obtained, was placed in a platinum dish, evaporated on a steam bath and dried at 110° C. Numerous comparisons showed that the same results were obtained as by drying at 100° C., and the time of drying, instead of being 12 to 24 hours, was reduced to 2 to 4 hours.

Table I gives the humus and the humus ash as obtained by the different methods, the percentages given in the tables being the average of two, and in most cases of three determinations:

TABLE I.—COMPARISON OF RESULTS OBTAINED BY DIFFERENT METHODS.

Method.	Soil No.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII
					Humus.	Per cent.								
Hilgard.....	2.22	1.64	1.01	1.61	1.61	0.85	7.31	0.71	0.57	9.53	0.49	0.41	0.45	
Huston-McBride.....	3.33	2.45	2.33	3.62	3.39	2.32	8.34	2.70	1.85	9.93	0.90	0.70	1.10	
Cameron-Breazeale.....	2.06	1.62	1.01	1.62	1.60	0.91	7.53	0.81	0.65	9.55	0.45	0.37	0.38	
Mooers-Hampton.....	2.07	1.63	1.03	1.60	1.56	0.92	7.47	0.79	0.63	9.56	0.50	0.36	0.43	
10 per cent. correction for ash.....	2.55	2.07	2.00	2.62	2.21	1.24	7.51	1.40	1.15	9.41	0.68	0.28	0.87	
14 per cent. correction for ash.....	2.23	1.88	1.86	2.22	1.74	1.81	7.20	0.89	0.87	9.21	0.59	0.11	0.78	
					Humus ash.	Per cent.								
Hilgard.....	0.44	0.67	0.76	0.84	0.47	0.67	2.72	0.35	0.67	1.35	0.29	0.30	0.20	
Huston-McBride.....	7.83	3.80	3.32	10.03	11.77	10.64	8.32	12.95	7.03	5.17	2.20	4.23	2.30	
Cameron-Breazeale.....	0.16	0.32	0.43	0.61	0.56	0.51	1.55	0.41	0.44	1.28	0.39	0.43	0.26	
Mooers-Hampton.....	0.71	0.27	0.42	0.29	0.27	0.39	0.55	0.12	0.20	0.71	0.13	0.08	0.20	

No. X. Surface foot from a bog near Fremont, Nebraska. The soil is so little above the level of the Platte River that it is saturated at all times of the year.

No. XI. A composite of surface six-inch samples from long cultivated fields near Pendleton, Oregon. The soil is commonly known as "volcanic ash," but is

The results for humus obtained by the Hilgard method in no case agree with those obtained by the Huston-McBride method, but in all cases they agree with those obtained by the two methods in which the clay is removed from the humus extract, viz., the Cameron-Breazeale and the Mooers-Hampton. In case of only Nos. VII and X does the humus found

by the Huston-McBride method approach that obtained by the Hilgard, being less than 15 per cent. higher, while in all other cases it is from 50 to 280 per cent. higher. In the case of all except Nos. VII and X, a correction of 10 per cent. of the humus ash gives results still much too high. When this correction is raised to 14 per cent. the results agree fairly well in some cases, but are too high in some and too low in others. When the data from individual determinations are considered, it is evident that in many cases the agreement of the averages is due to low results being counterbalanced by high ones.

The so-called "humus ash" shows still more variant results than does the humus. The amount found by the Huston-McBride method varies from 4 to 38 times as much as that found by the Hilgard. In general, the higher the ratio of ash to actual humus, the greater is the error in the amount of humus found by the Huston-McBride method. In the majority of cases less ash is found by the Cameron-Breazeale method and still less by the Mooers-Hampton than by the Hilgard. There is no definite relation between the humus and the ash, the latter varying by 100 per cent. in the case of duplicate determinations in which the results for humus agree.

*The Hilgard Method.*—The importance of a thorough examination of the method which has been used by Hilgard is due less to the probability that it will be used extensively in the future than to the fact that upon it depends the value of so much of his work upon humus. For this reason it is important to consider just how he, himself, has used the method. In practice he has continued the treatment with ammonia until the washings were colorless or so nearly so that the undissolved humus would make no appreciable difference in the results. This is indicated in his letter to Huston<sup>1</sup> in April, 1892. Although it is not specifically stated in the various publications describing his method,<sup>2</sup> it should be self-evident that when the soil is being washed with ammonia in order to dissolve out the *matière noire*, the washing should be continued until the ammonia no longer brings away any "black matter" as indicated by the color. After one has familiarized himself with the method he can judge from the intensity of the color of the washings whether enough humus remains to cause an appreciable difference in the results. That ten days or even longer may be required to complete the extraction in the case of some soils we have found to be true, but this does not at all invalidate the accuracy of the method. Hilgard, himself, regularly reported the amount of humus ash. He obtained the filtrates clear, before transferring them to the platinum dishes for evaporation. In a private communication, in 1907, he stated that where his stu-

dents obtained turbid solutions he had them make use of a Pasteur-Chamberland filter before evaporation—a practice which, as shown below, does not introduce any error.

TABLE II.—AGREEMENT OF DIFFERENT DETERMINATIONS BY THE HILGARD METHOD.

Soil No.		I	II	III	Av.	Difference	
						Humus	Ash
I.	Humus.....	2.26	2.21	2.19	2.22	3.3	
	Ash.....	0.61	0.43	0.27	0.44		126
II.	Humus.....	1.69	1.60	.....	1.64	6.0	
	Ash.....	0.68	0.65	.....	0.67		8
III.	Humus.....	0.98	1.05	1.00	1.01	7.0	
	Ash.....	0.74	0.77	0.76	0.76		4
IV.	Humus.....	1.60	1.62	1.60	1.61	1.0	
	Ash.....	0.83	0.78	0.91	0.84		16
V.	Humus.....	1.58	1.64	.....	1.61	4	
	Ash.....	0.39	0.55	.....	0.47		41
VI.	Humus.....	0.83	0.86	.....	0.85	4.0	
	Ash.....	0.70	0.63	.....	0.67		11
VII.	Humus.....	7.30	7.32	7.33	7.31	0.0	
	Ash.....	2.95	2.77	2.44	2.73		21
VIII.	Humus.....	0.67	0.73	0.72	0.71	9.0	
	Ash.....	0.31	0.47	0.26	0.35		81
IX.	Humus.....	0.59	0.56	0.57	0.57	5.0	
	Ash.....	0.58	0.67	0.77	0.67		3
X.	Humus.....	9.46	9.60	9.53	9.53	2.0	
	Ash.....	1.38	1.33	.....	1.35		4
XI.	Humus.....	0.49	0.49	0.50	0.49	2.0	
	Ash.....	0.27	0.30	0.30	0.29		10
XII.	Humus.....	0.44	0.41	0.37	0.41	19.0	
	Ash.....	0.37	0.30	0.24	0.30		54
XIII.	Humus.....	0.44	0.43	0.47	0.45	9.0	
	Ash.....	0.25	0.19	0.16	0.20		56

Table II shows the agreement of duplicate determinations by the Hilgard method, where extreme care had been taken to not only wash out all the humus, but also to avoid any of the clay being carried over the edge of the filter. Further, these determinations were made by those who had had much experience with the method and they, accordingly, are more concordant than the results obtained in the ordinary course of analysis. The variation between different determinations of the same soil is indicated in the last two columns of the table, in which is shown the relation of the difference to the lowest individual determination. For the humus this varies from 0 to 19 per cent. with an average of 5.5, the greatest difference being shown by a soil poor in humus. The humus ash shows a variation of from 3 to 126 per cent., with an average of 33.2. There is no relation between the agreement of duplicate determinations of humus and that of the corresponding duplicates of ash.

As the results in the above table are not representative of the results of ordinary analyses, the following two summaries are given, they having been obtained without reference to testing the reliability of the method. In one series of 30 soils with a humus content varying from 0.54 to 1.53 per cent., the maximum difference between either one of the duplicates and the average of the two was 15 per cent. of the lower result, while the average difference was 3.5

<sup>1</sup> Bull. 38, Bur. of Chem., p. 84 (1893).

<sup>2</sup> Ibid., p. 80; J. A. C. S., 16, 34 (1894); Circular No. 6, Univ. of California (1903).



per cent. In another series of 18 soils containing from 2.80 to 3.50 per cent. of humus the differences were 8 and 4 per cent., respectively.

Where the ammonia solution was applied continuously to the prepared soils until the washings were colorless, the extraction was in some cases incomplete, but when the soil near the end of the operation was allowed to stand some time between successive washings, the extraction could be carried to completion. Samples of the 13 soils, in sets of four, five or six each, were subjected to the continuous application of 4 per cent. ammonia solution until the washings became colorless. Then the receivers were replaced by others and ammonia added to the residues at wide intervals, until after standing 24 hours without washing, an application of ammonia gave a colorless filtrate. Determinations were made of humus and ash obtained both previous and subsequent to the change of receivers. Even where the second filtrate obtained by the continued washing with ammonia was colorless, it was evaporated in a platinum dish and the latter dried, weighed, ignited and weighed again. The approximate average lengths of time required for the different soils is shown in Table III. The time required to obtain a colorless filtrate by continuous washing varied from 3 to 90 hours. In the case of soil No. X, 19 days' additional treatment was required in order to remove the last trace of the humus.

TABLE III. SUCCESSIVE EXTRACTIONS OF THE SAME SOILS

	First extraction. Hilgard method.			Second extraction. Hilgard method.			Third extraction. Moore's-Hampton method.		
	Time.	Humus.	Ash.	Time.	Humus.	Ash.	Humus.	Ash.	
	Hrs.	Per cent.	Per cent.	Days.	Per cent.	Per cent.	Per cent.	Per cent.	
I	10	2.12	0.41	3	0.10	0.03	0.00	0.00	
II	5	1.36	0.65	4	0.08	0.02			
III	5	1.01	0.76	1	0.00	0.00	0.00	0.00	
IV	8	1.32	0.82	5	0.09	0.02	0.01	0.00	
V	8	1.84	0.46	5	0.07	0.01	0.00	0.00	
VI	5	0.83	0.67	1	0.00	0.00	0.00	0.00	
VII	40	6.71	2.39	7	0.60	0.13	0.09	0.02	
VIII	4	0.64	0.34	5	0.07	0.01	0.00	0.00	
IX	3	0.55	0.67	5	0.02	0.00			
X	90	8.96	1.25	19	0.54	0.12	0.17	0.02	
XI	5	0.49	0.29	3	0.00	0.00	0.00	0.00	
XII	64	0.34	0.23	7	0.07	0.07	0.00	0.01	
XIII	4	0.36	0.15	11	0.09	0.05	0.00	0.03	

In the case of the soils other than Nos. VII and X, the additional amounts of humus obtained by the continued extraction were not greater than the differences between duplicate determinations. The individual determinations made at the change of receivers agreed almost as well as those indicated in Table II, where all had been carried to exhaustion. The effect of the continued extraction, however, was to lessen the differences, that member of a set of three which showed the smallest amount of humus at the change in receivers unusually giving the most in the second extraction. The increase in ash was in all

cases very slight and in most cases too slight to be detected.

All the residues, except those of Nos. II and IX, were, after the above exhaustive extraction, transferred to flasks and treated with 4 per cent. ammonia solution, etc., by the Mooers-Hampton method, as though they had been fresh soils. This gave any of the particles of humus not previously reached by the ammonia an opportunity to dissolve and also subjected the whole of the remaining organic matter to 36 hours' contact with fresh ammonia. The averages of the determinations are shown in the last two columns of Table III. Only Nos. VII and X gave any humus in the extraction. Before the large amount of suspended clay was removed by the evaporation and subsequent filtration it was not possible to decide from the color whether any humus had been dissolved by this last treatment. The increase for No. VII was only 1 per cent. and for No. X only 2 per cent.

To determine what is the effect of filtration through a Chamberland-Pasteur filter upon the Hilgard humus extract, we made use of the humus extracts obtained by continuously applying ammonia to the soils until the washings were colorless. Accordingly the results are not to be compared with those in Table I, but with those in the third and fourth columns of Table III. In this case equal portions of the extracts from two or three samples of each soil were combined to form a composite which was passed through a filter prepared as follows: A new Chamberland-Pasteur filter, or one that had been burned out in the furnace after it had last been used, was washed with 4 per cent. ammonia, as described below, until 100 cc. of the filtered ammonia solution, when evaporated in a platinum dish, left no residue. The composite extract was then passed through this filter and three aliquot portions used for the humus determinations. The results of the three determinations, as was to be expected, agreed very closely with one another. The averages compared with those of the unfiltered extracts are shown in Table IV. While in two cases there is a distinct loss of ash due to filtra-

TABLE IV. EFFECT OF THE CHAMBERLAND PASTEUR FILTER UPON HUMUS SOLUTION

Soil No.	Before filtration.		After filtration.		Loss	
	Humus. Per cent.	Ash. Per cent.	Humus. Per cent.	Ash. Per cent.	Humus. Per cent.	Ash. Per cent.
I	2.12	0.41	2.07	0.44	0.05	-0.03
II	1.36	0.65	1.36	0.68	0.00	-0.03
III	1.01	0.76	0.99	0.70	0.02	0.06
IV	1.32	0.82	1.55	0.39	-0.03	0.43
V	1.84	0.46	1.53	0.49	0.01	-0.03
VI	0.83	0.67	0.83	0.52	0.02	0.15
VII	6.71	2.39	6.68	1.75	0.03	0.84
VIII	0.64	0.34	0.65	0.34	-0.01	0.00
IX	0.55	0.67	0.55	0.66	0.00	0.01
X	8.99	1.23	8.94	1.51	0.05	-0.28
XI	0.49	0.29	0.48	0.31	0.01	-0.02
XII	0.34	0.23	0.32	0.15	0.02	0.08
XIII	0.36	0.15	0.30	0.21	0.06	-0.06

tion, the changes in humus are not greater than the experimental error. Accordingly, a Chamberland-Pasteur filter so prepared may be considered to have no effect upon the amount of humus, although it lowers the ash in many cases.

*The Huston-McBride or "Official" Method.*—The analyses were conducted according to the directions in the "Official and Provisional Methods of Analysis of the Association of Official Agricultural Chemists,"<sup>1</sup> except that instead of using a Gooch crucible for the preliminary treatment of the soils with acid and distilled water, we used ordinary filters in funnels provided with protecting discs of filter paper, and instead of glass-stoppered cylinders we in most cases employed glass-stoppered, graduated flasks. The use of Gooch filters had not been found economical of time when working with many samples, and numerous comparisons of the cylinders with flasks had shown that where the soils stood in contact with the ammonia solution for 36 hours the shape of the vessel made no difference in the results. With peaty soils, however, there might be an advantage in using cylinders.

The differences between duplicates were greater in the case of the humus and less in that of the ash than those found in the Hilgard method. The maximum difference in humus between duplicates was 73 per cent. of the lower while that in ash was 70 per cent., the average difference being 17 and 40 per cent., respectively, against 5.5 and 33.0 in the Hilgard method. The differences between the amounts of humus obtained by the two methods are great and bear no definite relation to the humus obtained by either method.

The success of the attempt to make satisfactory corrections for the data from the Huston-McBride method would be dependent upon the percentage of ash being stated. Even with the ash given, the factor to be used would vary with different soils and to a considerable extent with the same soil. Thus, from Table I it will be seen that for soil No. III a correction equal to 40 per cent. of the ash is necessary, while for X one of only 8 per cent. is necessary. As pointed out above, even where 14 per cent. seems satisfactory for the average of two or three determinations, this is often due to the wide variation in ash between the different determinations. Thus, in the case of No. VIII, the average for the three determinations is 0.89 per cent. of humus, which is not so far from the 0.71 per cent. found by the Hilgard method. This fairly satisfactory average, however, is obtained from three determinations which gave 1.41, 0.72 and 0.53 per cent., respectively.

As Huston and McBride have stated, soils extracted by the Hilgard method give an additional loss on ignition (called by them *humus*) when treated by their method. Ten samples of No. 1433, ex-

tracted by the Hilgard method, were subjected to treatment by the Huston-McBride method. The results ranged from 0.37 to 0.62 per cent. of humus and from 1.44 to 2.01 per cent. of ash. Five other soils were similarly treated. Although the ammonia was not colored by freshly dissolved humus, the large amount of clay held in suspension caused a loss on ignition, after the second extraction, about equal to that after the first, as shown in Table V:

TABLE V.—TREATMENT OF RESIDUES FROM HILGARD METHOD BY HUSTON-McBRIDE METHOD.

Soil No.	First extraction. Hilgard.		Second extraction. Huston-McBride.	
	Humus. Per cent.	Ash. Per cent.	Humus. Per cent.	Ash. Per cent.
902	2.68	0.44	1.25	5.77
911	1.24	0.26	1.83	10.51
915	1.80	0.35	1.76	10.66
916	1.91	0.62	2.07	12.06
917	1.88	0.41	1.92	11.21
1433	0.82	0.25	0.37	1.44
			to	
			0.62	2.01

*The Cameron-Breazeale Method.*—We used the apparatus devised by the U. S. Bureau of Soils for the Chamberland-Pasteur filter, forcing the solution through the filter by means of compressed air. On the pressure cylinders, which were silver-plated, the plating was so thin that it was necessary to coat the inside of the cylinder with paraffine to prevent the solution of copper.

The humus extracts were prepared by the official method and a composite sample of the extracts was made by combining equal volumes. The Chamberland-Pasteur filter was washed with distilled water, after which 4 per cent. ammonia solution was forced through until a portion of the filtrate, on evaporation, gave no residue. Then 300 cc. of the composite humus extract was forced through the filter and the filter washed by forcing through 4 per cent. ammonia solution until the washings were colorless. Filtrate and washings were made up to a definite volume and aliquot portions used for the three determinations in the case of each soil. The averages of the three, which were in all cases concordant, are given in Table I. The percentages of humus agree with those found by the Hilgard method, but the ash is in most cases much lower. While this method, when carried out as just described, gives satisfactory results, it is so much more tedious than either the Hilgard or the Mooers-Hampton method that it is not to be recommended. Unless the above precaution be observed, the results are not to be relied upon.

*The Mooers-Hampton Method.*—The percentages of humus obtained by this method agreed within the limits of experimental error with those obtained by the preceding method, but the ash was in most cases much lower. The duplicate determinations of humus agreed well, the percentage difference varying from 1 to 15 per cent. with an average of 5.7. As in the

<sup>1</sup> Bull. 107, Bur. of Chem., p. 19 (1908).

case of the Hilgard method, the ash showed a much greater variation, ranging from 0 to 164 per cent. with an average of 41.

*The Snyder Method.*—As this method appears to have been used by no one except the author of it, and as it offers no particular advantages over the Hilgard and the Mooers-Hampton methods, we gave it a careful test with only a single sample of soil, one from the loess of eastern Nebraska. The results were as follows:

SNYDER METHOD.			
	1.	2.	Average.
Humus.....	2.44	2.38	2.41
Ash.....	1.56	1.58	1.57

MOOERS-HAMPTON METHOD.			
	1.	2.	Average.
Humus.....	2.21	2.34	2.27
Ash.....	0.23	0.33	0.28

This indicates that the method can be used to obtain results comparable with those of the other reliable methods. It is, however, likely in unpractised hands to give too high results.

*The Influence of the Strength of the Ammonia Solution.*—Huston and McBride<sup>1</sup> reported experiments made to determine the influence of the strength of the ammonia solution upon the amount of humus dissolved. They used the Hilgard method, as well as their own, with ammonia solutions of 2, 4, 7.3 and 8 per cent. Their results, in general, indicated that the stronger the ammonia the more humus was dissolved. This was not an unvarying rule, however.

We have tried ammonia solutions of the strengths of 2, 4, 8, 16 and 28 per cent. in the Mooers-Hampton method. The six soils used were similar to Nos. I to IX, but on account of our supply of Nos. II to IX being exhausted, similar, instead of identical soils were used. Two or three determinations were made in the case of each soil. The averages are shown in Table VI.

Soils Nos. XIV, XV, XVI, XVII and XVIII are similar to Nos. II, VII, VIII, VI and III, respectively, having been taken from the same localities and to the same depths:

TABLE VI.—COMPARISON OF RESULTS USING AMMONIA SOLUTIONS OF DIFFERENT STRENGTHS.

Soil No. I. XIV. XV. XVI. XVII. XVIII. Average.									
Strength of ammonia solution.		Humus. Per cent.							
2 per cent.....	2.01	1.72	6.53	0.53	0.94	1.26	2.16		
4 per cent.....	2.12	1.82	6.34	0.60	1.16	1.39	2.24		
8 per cent.....	2.16	1.85	6.28	0.62	1.12	1.40	2.24		
16 per cent.....	2.34	2.06	6.62	0.67	1.17	1.64	2.42		
28 per cent.....	2.34	2.14	6.63	0.71	1.23	1.17	2.47		
		Humus ash. Per cent.							
2 per cent.....	0.36	0.19	1.72	0.23	0.19	0.38	0.51		
4 per cent.....	0.41	0.26	1.39	0.21	0.20	0.43	0.47		
8 per cent.....	0.33	0.23	0.39	0.08	0.18	0.24	0.33		
16 per cent.....	0.38	0.34	0.87	0.18	0.21	0.16	0.36		
28 per cent.....	0.30	0.33	1.15	0.16	0.32	0.21	0.41		

In all but one case more humus was dissolved by 4 per cent. ammonia solution than by 2 per cent. Practically the same amount was dissolved by 8 per cent. as by 4 per cent.; more by 16 per cent., and in most cases, still more by 28 per cent. It is evident from the table that slight variations in the strength of the ammonia solution above or below 4 per cent. are not of much consequence. The amount of ash varied independently of the strength of the ammonia.

#### SUMMARY.

1. The Hilgard, Huston-McBride, Cameron-Breazeale and Mooers-Hampton methods for the determination of humus were compared, using arid, semi-arid and humid soils.

2. The Hilgard method, as used by its author, was found to give entirely reliable and satisfactory results. In the case of soils rich in humus and those of very fine texture the method is at times very tedious.

3. The Huston-McBride or "official" method gives results which are entirely unreliable and which, in the case of most soils, are far too high. The errors incidental to the method are of such a nature that it seems impossible to apply to the results any satisfactory correction formula.

4. The humus extract obtained by the Huston-McBride method, after being passed through a properly prepared porcelain filter, gives results which are concordant with those obtained by the Hilgard method.

5. The Mooers-Hampton modification of the Huston-McBride method gives results entirely concordant with those of the Hilgard method. For some soils it is preferable to the latter, requiring much less time.

6. Ammonia solutions of different strengths were not found to have the same solvent power for humus. The differences, for strengths between 2 and 8 per cent. were slight, but where solutions of from 16 to 28 per cent. were used considerably more humus was dissolved.

7. The amount of so-called "humus ash" found in the case of a soil sample varies from method to method and bears no relation to the strength of the ammonia used. There is little or no agreement between duplicate determinations of the "humus ash." From 4 to 38 times as much ash is obtained by the Huston-McBride method as is obtained by the other methods. It is probable that the greater portion of the "humus ash" obtained by any of the methods is not an essential part of the humus.

8. In reporting the humus the per cent. of "humus ash" should always be reported, as it serves as an indication of the reliability of the humus determination.

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## OPTICALLY ACTIVE NON-SUGAR OF THE SUGAR BEET.

By W. H. REES.

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During the past two years considerable attention has been paid in European countries to the cause of excessive unaccountable loss of sugar in beet sugar factories. The reason of this has been attributed to climatic conditions which have developed a new substance in the beet that is optically active and is either eliminated or destroyed in the processes of the factory. To the present time, however, no one has published an account of having definitely determined just how, or where, in the process, this loss occurs; or of having obtained from the beet or factory products a dextro-rotatory substance which would be destroyed or eliminated by the factory processes. A summary by K. Andrlík, of the published articles concerning the existence of such a dextro-rotatory substance, was published in the *Zeitschrift für Zuckerindustrie in Böhmen*, August, 1909. In the October and November, numbers, 1909, Dr. O. E. Kopecký has fully described his experiments along this line, extending over a period of eight years, and has left little room for doubt that there has been present in the beets on which he worked a substance that indicated a higher per cent. of sugar by the direct method of estimating sugar than by the inversion method. In the same Journal, December, 1908, Ing. Fr. Herles describes his experiments in which he found that the action of lime and heat on beet juice caused a reduction in the polarization (this report is supplemented in Andrlík's article above referred to), and while Herles has been unable to satisfy many chemists as to the truth of his discovery, he has, in accordance with my experience, undoubtedly located the station where the greatest apparent loss of sugar occurs.

As shown by irregularities in factory and laboratory work, this substance has been present in the beets of the Alameda Sugar Company, Alvarado, Cal., for the past five years, and for the past three years in disturbing influence has been very marked. In January of 1909 the author began experiments to search for some optically active non-sugar which would explain the results of observation made in the campaign of 1908, and was soon rewarded by obtaining from the evaporator thick juice a dextro-rotatory substance which was not precipitated by basic lead acetate in water solution and gave a dextro-rotation in acid, alkaline, and neutral solution.

This substance was first obtained from the evaporator thick juice, later from the molasses, and afterward from the evaporator condensation water produced during the concentration of the osmose syrup.

Throughout the inter-campaign all of the spare time was spent in extracting and experimenting with

this substance, but at no time did the specimen obtained appear to be pure, and in quantity enough, to attempt an analysis to determine the composition of the rotatory substance. Naturally, small quantities had to be worked with, and after the extraction and numerous washings necessary to free it from the adhering substances there was very little left. A solution was obtained from one experiment which, when concentrated and then diluted to just fill a 200 mm. tube, gave a reading of  $30^\circ$  to the right. It has been extracted from the molasses of 1904, 1905, 1907, and 1908, and from the beet and factory products of 1909.

As obtained, the following properties have been ascribed to it:

It may be considered as an acid, or a substance which, like sugar, can be combined with calcium or lead. The solutions which have contained it free from bases have been faintly acid to phenolphthalein, but this acid may not be the rotatory substance. It was found to be very difficult to free the solution from acetic acid.

It is, in a free condition, easily soluble in water, alcohol and acetone, but insoluble in ether.

The lead compound, produced by basic lead acetate, is soluble in water and dilute alcohol and quite soluble in strong methyl alcohol, but almost insoluble in ethyl alcohol of 85 per cent.

The calcium and sodium compounds are readily soluble in water, and also in dilute alcohol, but practically insoluble in absolute alcohol. Much more soluble in strong methyl alcohol than in strong ethyl alcohol.

As obtained from the thick juice of 1908, and the evaporator condensation water from the osmose syrup it is not destroyed by heating with dilute mineral acids, neither is it destroyed by the usual inversion method of heating for five minutes at  $68^\circ$  C. with concentrated hydrochloric acid, but long heating in such acid renders it inactive. Strong acetic acid destroys it readily when heated on the water bath at  $70^\circ$  C.

By heating on the water bath with milk of lime it loses its optical activity entirely, but if slowly evaporated in slightly alkaline solution it does not lose this property, and when evaporated to dryness from a neutral solution it may be heated to  $110^\circ$  C. for hours without changing its rotatory power.

It is not volatile but can be carried over from a dilute acid solution, by distilling with a current of steam.

It does not reduce Fehling's solution and is not destroyed by alcoholic fermentation.

No signs of crystallization have been observed, and in the nearest approach to purity that it has been obtained, it was of a light amber color, in appearance resembling very closely light-colored gum arabic, but completely soluble in absolute alcohol.

The lead compound, after thorough washing, is soluble in an excess of lead acetate. If, however, it is dried, it then becomes insoluble in lead acetate, but on boiling with water and decomposing with  $H_2S$  a dextro-rotatory solution is obtained, which is not destroyed by heating with strong hydrochloric acid.

The substance obtained directly from the beet is apparently more readily affected by acid than that obtained from molasses, or from the condensed water from evaporating osmose syrup.

My experience with this substance leads me to believe that either it exists in the beet as a complex, unstable compound, which readily breaks down into products of lower optical power and quite stable, or that we have originally two closely allied substances, one of which readily changes and loses its power to rotate light, while the other is more stable and requires vigorous treatment to change its properties.

The fact that its lead compound is practically insoluble in strong alcohol affords a ready method for obtaining it directly from the beet. And the fact that this lead compound is readily soluble in dilute alcohol accounts for the agreement of water and alcohol digestions when made by the usual methods.

If finely grated beets are extracted with 90 per cent. alcohol and basic lead acetate added to the clear solution thus obtained, there will be produced a yellowish white precipitate. If this procedure is carefully carried out, it will be found that the polarization of the alcoholic solution before the addition of lead acetate will correspond very closely to the polarization of the water digest made with the requisite amount of lead acetate. It will also be found that the polarization of the alcoholic solution after the addition of the lead acetate and the proper correction for dilution is considerably lower than that of the water digest. This, so far as I am aware, has been attributed to the precipitation of sugar by the lead acetate in alcoholic solution. A pure sugar solution, in the same strength of alcohol, will not yield a precipitate when lead acetate is added, unless a very large excess is used. In the case of the beet juice in alcohol, it is found that if the addition of the lead acetate is cautiously made and time allowed for the separation, a point will be reached when the further addition of the reagent does not cause further precipitation. If, at this point, the precipitate is filtered off and thoroughly washed with alcohol containing a little lead acetate and afterwards with water, then boiled with water and  $H_2S$  passed in, the lead is precipitated as sulphide, and after cooling and filtering a solution is obtained which turns the ray of light to the right. By the addition of alcohol and lead acetate to this solution, a precipitate is again formed. If this is washed with alcohol and lead acetate until a 400 mm. tube, filled with the washings,

gives a rotation so slight as to be scarcely definable, then the residue boiled with water and decomposed with  $H_2S$ , the solution obtained is dextro-rotatory and remains so after heating for five minutes with concentrated hydrochloric acid.

The differences between the polarization of water digest and the alcohol digest, maintaining an alcoholic strength of 85 per cent., have generally been greater than the differences between the direct and inversion polarizations, and in my determinations I have not been able to obtain a quantitative separation which would agree with the difference between the water and alcohol digest, though in one carefully carried out test, in which an accumulation of several precipitates was used, the results were not far from the results obtained by inversion.

By carefully carrying out comparative estimations of the sugar in the beets and the various products of the factory, by the use of water solutions and alcoholic solutions of 85 per cent. to 90 per cent., it has been shown that there is a continual diminishing of the differences between the polarizations of the water and alcoholic solutions, from the entrance of the beets to the factory until the juice has passed through all of the saturation stations and that afterward there is not the increase in these differences that we should have, as these saturation juices are concentrated to fillmass. This has been shown also by the inversion method of estimating the sugar. The results of determinations made during the last campaign show differences ranging from nothing to as much as one and one-half per cent. in the beets and beet juices, and averaging less for the diffusion juice than for the beets, while the differences in polarizations of water and alcohol solutions of the first saturation juices was seldom over two-tenths of one per cent. If after the defecation by lime there was no further loss of this dextro-rotatory substance, it should occur (owing to the concentration) in the final molasses in quantities indicating two or three per cent. of sugar, but this has not been found to be the case, the average being only about six-tenths of one per cent.

As previously stated, this dextro-rotatory substance has been obtained from the evaporator condensation water when concentrating the osmosed syrup, and in the campaign of 1909, the vapors escaping from the first liming or defecation pan were condensed, and from these condensed vapors a dextro-rotatory substance was extracted. By greatly concentrating the condensation water from the evaporators, I was able to get it from this also, but in very small amounts. Especially interesting in connection with the water solution obtained from the condensation of the vapors from the lime pan, was the fact that as it was concentrated, it gradually became brown, and from an almost colorless solution it changed

to a dark brown mass of the consistency and color of beet molasses, and decomposed as it was concentrated on the water bath, yielding a brown powder insoluble in water. In this respect, it conducted itself like the free acids obtained when extracting the first specimen of the dextro-rotatory substance from the evaporator thick juice. The presence of this dextro-rotatory substance in the vapors readily explains why we do not have the increased differences between the polarizations of water and alcoholic solutions of the thick syrup, filmasses, and molasses, that we should naturally expect to have by concentrating the thin juices. This may also explain a long-existing question, Why do we always have an apparent loss of sugar during the evaporation and pan boiling of sugar solutions?

The theory first advanced by different writers on this subject, as to the cause of the presence of this particular dextro-rotatory substance in the sugar beet, viz., the weather conditions of the past few years does not appear to be well grounded. From the properties thus far obtained, and a review of the various methods proposed by different analysts in their efforts to establish a uniform and correct method for estimating the sugar in the beet, we find good evidence to indicate that it has always been a constituent, and that the increased percentage in the beets of the present day is more than probable, largely the result of seed selection, although it may be that the quantity is altered by the weather conditions. During the campaign of 1909 it was found in beets from widely different localities, where seasonal and climatic conditions were entirely different. It was found in beets grown at sea-level and those grown at several thousand feet elevation, in beets grown without rain or irrigation and in beets grown with both rain and irrigation. It has also been found in beets that have had a second growth and have remained in the ground all winter. From all of these various conditions the differences have not varied materially more than from the beets taken from the same field at the same time. It thus appears that locality and climatic conditions are not the primary cause for the presence of this dextro-rotatory substance in the beets.

In conclusion, I wish to say that my experience has fully convinced me that the observations of Dr. Kopecky, and other chemists who have found differences between the polarizations by the direct and by the inversion methods, have been correct, and that the probable reason why these differences have not been greater in many cases, and why other chemists have failed to find any such differences, has been due to the destructive action of the acetic acid liberated from the lead acetate by the hydrochloric acid, added for the inversion. Also, my work has shown that the discovery of Ing. Fr. Herles that there is a

reduction of the polarization of the beet juice and diffusion juice, when they are heated with lime, and also that it is possible to precipitate this substance by lead acetate in very strong alkaline solution, as with caustic lime and basic lead acetate in combination, is correct.

It is my intention to continue the study of this substance and, if possible, to ultimately determine its composition.

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## THE INFLUENCE OF MICRO-ORGANISMS UPON THE QUALITY OF MAPLE SYRUP.

By H. A. Edson.

Received April 23, 1910.

In certain climates and under specific weather conditions in the spring of the year, a flow of sap occurs from fresh wounds in the twigs and trunk of certain trees of the *Acer* genus. By evaporation to the proper consistency of the sap of certain species, particularly the rock or sugar maple, *Acer saccharum* Marsh, syrup and sugar are obtained. A detailed discussion of the conditions governing sap flow is given in *Bull.* 103 of the Vermont Agricultural Experiment Station. It is sufficient, at this time, to note that the sap is obtained only during the three or four weeks which immediately precede the unfolding of the leaf buds, and that the flow is intermittent, being divided into what are technically termed runs. Freezing nights, followed by a temperature somewhat above 40° F. during the day, and the absence of heavy winds and excessive sunshine, afford the best sugar weather. The sap is obtained by boring a hole 1/2 inch in diameter and 1 1/2 to 2 inches deep in the trunk of the tree and inserting a round hollow spout, preferably of metal, upon which is hung a bucket to receive the sap as it flows, drop by drop, from the wound. It is gathered after each run and concentrated as rapidly as the facilities of the boiling house will permit.

The appearance of the sap undergoes a marked change as the season progresses. That first obtained is clear and transparent and possesses a delicious sweet flavor, but with the advance of the season, as the days become warmer and the freezing nights less severe and less frequent, the sap often becomes cloudy and discolored and certain unpleasant flavors develop. Such sap, while usually free from acid, is popularly termed sour. Several types of this sour sap are recognized by sugar-makers. Milky sap, stringy sap, red sap, and particularly so-called green sap are among the more common kinds. Green sap is almost always observed just before the close of the season, when the leaf buds are ready to open, and it is a matter of popular belief that the swelling of the buds is accompanied by a change in the sap within



the tree trunk, manifestations of which are the changes in color and taste. The term "Buddy" is in universal use to describe such material.

Accompanying this change in the sap there occurs a deterioration in the quality of syrup produced, the early product being much superior to that obtained late in the season. Last-run material is often very dark in color and usually lacks the delicate flavor possessed by the best goods. Moreover, the quality varies markedly from year to year, and these variations are seldom local in distribution. It is also a matter of general knowledge that uncleanly methods yield poor syrup.

A consideration of the above facts suggested the idea that micro-organisms may be the direct cause of the trouble in all these cases. More favorable weather conditions in poor years and at the close of the season might result in the rapid increase of germ life in the tap hole, spout and bucket, thus producing a heavy inoculation. Uncleanly methods will certainly result in this condition. Accordingly, in the spring of 1907, studies of the microscopic flora of maple sap were undertaken to determine, among other points, the influence of these organisms upon the quality of syrup. A preliminary report upon the work is soon to appear from the Bacteriological Department of the Vermont Agricultural Experiment Station.<sup>1</sup> Only results which will more particularly interest food chemists are included in this paper.

In the preliminary studies it was shown that the sap within the vascular bundles of the tree is free from micro-organisms. When drawn under conditions which prevent their entrance the sap keeps perfectly without being subjected to sterilization or the use of preservatives, whereas sap drawn under ordinary conditions promptly becomes cloudy and undergoes decomposition changes. Examined by the usual bacteriological methods, such material is found to be swarming with bacteria, yeasts, and the spores of molds. During the first season's work a careful study was made of the organisms in each of the more common types of sour sap. The predominant organisms in each were isolated and studied in pure culture. The following spring, inoculations were made into sap obtained from the first run. The character of the changes produced in the sap both as regards appearance, flavor, and reaction, were noted, and after three days' incubation the materials were evaporated to syrups under uniform conditions, and the products compared with controls. The syrups were scored as to color and flavor by a professional who was unfamiliar with their history, and the percentage of sucrose and invert sugars were determined by chemical analysis. For convenience in discussion, the inoculation experiments are divided into series.

Series A contained seven samples. Six of these

(Nos. 7-12 inclusive) were inoculated each with different pure cultures of green fluorescent bacteria isolated from green sour sap. The other (No. 2) was reserved as a control on Series A, B, and C. Within a few hours after inoculation typical green sap began to develop, and as incubation proceeded a foul or slightly bitter taste became apparent. Titration of 100 cc. portions with N/100 alkali before and after incubation revealed no change in reaction. Samples incubated in fermentation tubes developed no gas. The syrups obtained were without exception dark brown in color, with a noticeable admixture of red. They were rated as No. 2 in both color and flavor. Figured on a dry matter basis, these syrups averaged 96.75 per cent. of sucrose and 1.57 per cent. of reducing sugar. The control sap remained clear and sweet. The syrup was a No. 1 product of light amber color and fine delicate flavor. It analyzed 95.41 per cent. sucrose and 0.97 per cent. reducing sugar.

The samples of Series B were inoculated with material obtained from cloudy sour sap. For purposes of comparison, a foreign organism isolated from stringy canned peas was added to this series. The type of souring produced was characteristic and similar in all cases except that the foreign organism was capable of acid and gas production. The syrups were somewhat cloudy in appearance but sufficiently light to be rated as No. 1 in color. The flavor, however, was very seriously impaired, being so unlike the natural maple flavor that one would be inclined to question the purity of the products. Syrups (Nos. 13 and 14) from sap inoculated with the true sap organism averaged 95.73 per cent. sucrose and 0.77 per cent. reducing sugar. Material (No. 15) inoculated with the acid-producing foreigner analyzed 95.71 per cent. sucrose and 2.23 per cent. reducing sugar.

Series C was inoculated with an organism believed to be a new species, obtained from a milky type of stringy sap. The typical stringy character developed strongly and a characteristic sour odor was very marked. Slight gas and acid production were obtained. The syrup (No. 16) was No. 1 in color but viscous and stringy in consistency and of very inferior flavor, being rated as No. 3. It contained 96.12 per cent. sucrose and 1.72 per cent. reducing sugar.

Series D was inoculated with yeasts and molds obtained from red sap and from various other sour samples. The characteristic cloudy appearances developed in these materials but neither acid nor gas production were present. The sap used in this series possessed a relatively high initial contamination, so that a part of the action must be attributed to micro-organisms other than those introduced by inoculation, but there is still a striking contrast between the

<sup>1</sup> "Buddy Sap," Bull., 151; Vt. Agr. Exp. Sta., April, 1910.

inoculated materials and the control. Four (Nos. 18, 19, 22, and 23) of the seven syrups of this series were rated as No. 2 in color, three (Nos. 17, 20, and 21) were rated as No. 1. Five of them (Nos. 17, 18, 20, 21, and 22) were rated as No. 2 in flavor and two (Nos. 19 and 23) as No. 3. The chemical analysis showed an average of 93.93 per cent. sucrose and 3.11 per cent. reducing sugar. The control of this series (No. 5) was rated as No. 1 in both flavor and color. It contained 95.37 per cent. sucrose and 1.58 per cent. reducing sugar.

As a further proof that the inferior color and quality of late-run sap is due to the fermentative action of micro-organisms in the spout and bucket, trees were selected late in the season from which sour sap was being obtained. These were tapped a second time on a level with the original wound and about 4 inches to one side of it. Clean buckets and spouts were employed at the new tap holes. The old buckets were emptied and rehung in their former places. In this way two different types of sap were obtained from the same trees at the same time. That from the old tap holes was cloudy and sour, while that from the new was perfectly clear and sweet. These were gathered separately and made into syrups. All the material (Nos. 3, 4, and 6) from the fresh tap holes was No. 1 in both color and flavor, being equally good with the material made from the control of the first run. The samples averaged 95.88 per cent. sucrose and 0.65 per cent. of reducing sugar. Of the samples from the old tap holes, two (Nos. 24 and 25) were rated as No. 2 in color and one (No. 26) as No. 3. This was the darkest sample obtained during the season's work. All three were No. 2 in flavor. They averaged 93.96 per cent. sucrose and 3.15 per cent. reducing sugar. Samples 3, 4, and 6 were obtained from the new tap holes at the same time, respectively, as were Nos. 26, 25 and 24 from the old. Nos. 3, 4, 26 and 25 were obtained during the same run, but 4 and 25 were evaporated at once while Nos. 3 and 26 were allowed to incubate one day before concentration. This accounts for the marked contrast in appearance between Nos. 25 and 26. The light initial inoculation in the fresh tap hole prevented the appearance of a similar contrast between Nos. 3 and 4.

Sample No. 1 was made from the sap used in Series A. It was handled exactly as was No. 2 except that three times as long was used in its evaporation. Attention is called to the fact that all of the samples reported in this paper conform to the maple syrup standard in spite of the methods of handling. The following table gives the summary of the analysis and scoring, together with the ratio of sucrose to reducing sugar.

SUMMARY.

Description of sample.	Sucrose.		Reducing sugar.		Color	Flavor
	Sample No.	Per cent.	Per cent.	Ratio		
Controls. . . . .	1	96.84	1.07	90	1	1
	2	95.41	0.97	98	1	1
	3	96.02	0.61	157	1	1
	4	96.42	0.51	189	1	1
	5	95.37	1.58	60	1	1
	6	95.19	0.82	116	1	1
Series A. . . . .	7	96.79	1.55	62	2	3
	8	96.73	2.09	46	2	2
	9	96.54	1.56	62	2	2
	10	97.16	1.44	67	1	2
	11	96.16	1.64	59	2	2
	12	97.14	1.15	84	2	2
Series B. . . . .	13	95.61	0.78	122	1	2
	14	95.86	0.77	124	1	3
	15	95.71	2.23	43	1	3
Series C. . . . .	16	96.12	1.72	56	1	3
Series D. . . . .	17	93.34	2.53	37	1	2
	18	95.30	3.01	32	2	2
	19	95.73	2.61	37	2	3
	20	93.26	2.98	31	1	2
	21	92.76	3.47	27	1	2
	22	91.65	3.12	29	2	2
Old tap hole. . . . .	23	93.28	4.09	23	2	3
	24	95.27	2.76	35	1	2
	25	94.05	3.13	30	2	2
	26	92.56	3.55	26	3	2

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[CONTRIBUTION FROM THE LABORATORY OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE RELATION BETWEEN FAT AND CALCIUM IN CREAM.

By HERMANN C. LYTHGOE AND CLARENCE E. MARSH.

Received May 11, 1910.

A number of analyses of samples of cream were made with a view of determining the largest amount of calcium which could naturally be present, and above which the addition of any compound of calcium could be declared. Upon looking over these analyses, it was noticed that the amount of calcium in the pure product varied considerably and was lowest in heavy cream and highest in light cream. A sample of cream was then obtained and was mixed in varying proportions with the skimmed milk from which it had been separated. The analyses of these samples showed that the addition of the skimmed milk increased the calcium in the mixed product, the amount being greatest in the sample having the lowest fat. A second series of analyses were made upon other mixtures of skimmed milk and cream with similar results.

The results of the analyses of a number of samples of cream are shown in the accompanying plot, the samples being obtained from the following sources:

1. Known purity samples, the cows being milked and the cream separated in the presence of an analyst of the Massachusetts State Board of Health (recorded with a cross).

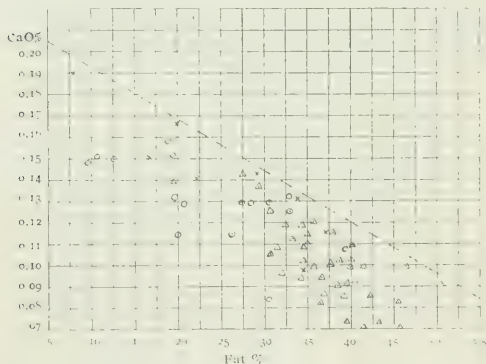
2. Samples separated in the laboratory from the milk collected by the inspectors of the department (recorded with a circle).

3. Commercial samples found free from cane sugar by the Baier and Neumann test<sup>1</sup> and also found free from preservatives (recorded with a triangle).

In making the analyses the fat was determined by the Babcock method and the calcium, and also the alkalinity of the ash, as follows:

Weigh 25 grams of cream into a platinum dish, place in an oven at about 125–150° C. over night and burn to an ash in a muffle at a low red heat. Dissolve the ash in 20 cc. N/10 sulphuric acid, boil to expel the carbon dioxide and titrate back with N/10 sodium hydroxide, using phenolphthalein as the indicator. Express results as cc. N/10 acid required to neutralize the ash of 100 grams of cream.

Make the final solution of the above determination acid with acetic acid, heat to boiling, add 1 gram of sodium acetate, and to the clear solution add an excess of ammonium oxalate, boil for a few minutes, filter and wash with water. Dissolve the calcium oxalate in hot dilute sulphuric acid and titrate hot with N/10 potassium permanganate. cc. N/10 permanganate multiplied by 0.0112 ( $4 \times 0.0028$ ) gives the percentage of CaO in the sample.



It will be seen from the plot that most of the known purity samples and those separated in the laboratory were relatively higher in calcium than the commercial samples. This is probably due to the fact that commercial cream is, as a rule, pasteurized, or is made from pasteurized milk. It is a well-known fact that pasteurizing milk renders some of the calcium insoluble, and experiments made in this laboratory show that cream of the same fat content made from the same milk, part of which has been heated, will contain less calcium in the heated portion.

The presence of calcium in less quantity than that shown by the maximum figures does not necessarily mean that the sample is free from calcium succrate.

For example, if a quantity of calcium succrate sufficient to thicken were added to a sample of cream having 30 per cent. fat and 0.085 per cent. calcium oxide, the calcium would be increased to about 0.11 per cent. or 0.13 per cent., or less than 0.144 per cent., which is the maximum amount which could be present in natural cream.

The following table shows the maximum amount of calcium oxide corresponding to the fat content in pure cream:

Fat Per cent.	Maximum CaO Per cent.	Fat Per cent.	Maximum CaO Per cent.	Fat Per cent.	Maximum CaO Per cent.	Fat Per cent.	Maximum CaO Per cent.
15	0.181	25	0.156	35	0.132	45	0.108
16	0.178	26	0.154	36	0.129	46	0.106
17	0.175	27	0.151	37	0.127	47	0.103
18	0.173	28	0.149	38	0.124	48	0.100
19	0.171	29	0.146	39	0.122	49	0.098
20	0.169	30	0.144	40	0.120	50	0.096
21	0.166	31	0.141	41	0.118	51	0.093
22	0.164	32	0.139	42	0.115	52	0.090
23	0.161	33	0.137	43	0.113	53	0.088
24	0.158	34	0.134	44	0.110	54	0.085

## FURTHER STUDIES OF THE REACTIONS OF LIME-SULFUR SOLUTION AND ALKALI WATERS ON LEAD ARSENATES.

By C. E. BRADLEY AND H. V. TARTAR.

Received April 18, 1910.

It was shown by us<sup>1</sup> that only very small quantities of arsenic were rendered soluble on mixing a neutral lead arsenate and commercial lime-sulfur in a combined spray. More recently we have noticed that the residue from the mixture of an acid arsenate was much darker in color than that from the neutral indicating that considerable decomposition or inter-reaction had taken place in the former instance. It was thought advisable, therefore, to make a comparative study of the reactions taking place and the product formed when either the acid or neutral arsenate of lead is mixed with the lime-sulfur solution under spraying conditions.

A sample of Niagara lime-sulfur having a specific gravity of 32° B. was selected for the tests. Bean's ortho arsenate of lead was taken as a representative of the neutral and Hemingway's arsenate as a type of the acid arsenate. Analysis in our laboratory had shown these arsenates to have the following composition:

COMPOSITION OF LEAD ARSENATES.

	Hemingway's Per cent.	Bean's Per cent.
Moisture .....	32.46	41.68
Total PbO .....	42.64	42.19
Total As <sub>2</sub> O <sub>3</sub> .....	21.45	13.47
Soluble As <sub>2</sub> O <sub>3</sub> .....	0.31	0.10
Soluble impurities .....	0.93	1.60
Total .....	97.48	98.94

The arsenates were in each instance added in the proportion of four pounds of the moist arsenate to

<sup>1</sup> Z. Naturforsch., 16, 51.

<sup>1</sup> THIS JOURNAL, 1, 8, 610.



one hundred gallons of the lime-sulfur diluted 1 to 30. The mixtures were agitated occasionally for twenty-four hours, then filtered and the residue washed and dried at 80° C., then at 100°. The residue from the acid arsenate was very dark in color from the lead sulfid present, while that from the neutral was gray, indicating but slight decomposition. A partial analysis of the filtrate from each arsenate gave results as follows, a blank consisting of untreated lime-sulfur being run for comparison:

COMPOSITION OF THE LIME-SULFUR SOLUTION BEFORE AND AFTER ADDITION OF LEAD ARSENATE.

	Blank lime-sulfur.	Grams per 1000 cc. Filtrate from acid arsenate and lime-sulfur.	Filtrate from neutral arsenate and lime-sulfur.
Total S.....	10.750	10.256	...
Total CaO.....	4.380	4.060	...
As <sub>2</sub> O <sub>5</sub> .....	...	0.095	0.012

The above results indicate that eight times as much arsenic is rendered soluble from the acid arsenate as from the neutral, or calculated to the original material this would be equivalent to 0.25 per cent. of soluble As<sub>2</sub>O<sub>5</sub> from the neutral and 1.98 per cent. from the acid. Distinct losses of sulfur and lime have also taken place in the acid arsenate mixture and it is evident that there is a mutual decomposition when lead acid arsenate is mixed with the lime-sulfur solution.

Analysis of the dried residues gives further evidence of the breaking down of the acid arsenate under these conditions:

ANALYSIS OF THE RESIDUE FROM THE MIXTURE OF LIME-SULFUR AND LEAD ARSENATE.

	Neutral arsenate residue. Per cent.	Acid arsenate residue. Per cent.
Free S.....	0.70	20.80
PbS.....	1.47	14.80
CaO.....	...	10.40

Sulfur was determined by extracting the dry residue with CS<sub>2</sub>; the lead sulfid by extracting the remaining residue with HNO<sub>3</sub> 1 : 10; the lime by precipitation as oxalate after removing lead and arsenic with hydrogen sulfid.

A study of the reactions involved in the above mixtures indicates that there is a partial interchange of the lime and lead resulting in the formation of calcium arsenate and lead sulfid respectively, free sulfur being at the same time deposited. The soluble arsenic is then derived from partial solution of the calcium arsenate thus formed. Sulfids of arsenic are not formed, as these sulfids are soluble in the alkaline lime-sulfur forming sulpho salts, and sulpho salts are not present in the solution. The reactions as shown above are much more pronounced with the acid than with the neutral arsenate and it is therefore advisable to employ the neutral form when desiring to combine lime-sulfur and lead arsenate.

Having found that the *alkaline* lime-sulfur solution

reacts quite readily with the *acid* lead arsenate, the tests were extended to determine the comparative solvent action of alkaline and saline waters on these arsenates.

Haedden has stated<sup>1</sup> that lead arsenate is more soluble in waters containing alkali salts than in normal water. In the tests which are reported in the succeeding table a quantity of the moist arsenate, equivalent to ten grams of the dry arsenate, was treated in each case with two liters of solution, except in case of the CO<sub>2</sub> test, in which two grams of the moist arsenate were used. The solutions were kept at room temperature (about 17° C.) for twenty-four hours with occasional shaking, then filtered and the filtrate analyzed for soluble arsenic by the modified method of Gooch and Browning,<sup>2</sup> 500 cc. equivalent to 2.5 grams of the arsenate being used in each determination. The alkali water used in the tests was the extract from a natural alkali incrustation containing 50 per cent. Na<sub>2</sub>SO<sub>4</sub>, 18 per cent. NaCl, 13 per cent. Na<sub>2</sub>CO<sub>3</sub>, and 2 per cent. NaHCO<sub>3</sub>. The arsenic is reported as per cent. of the original material:

SOLUBLE ARSENIC PENTOXIDE FROM NEUTRAL AND ACID LEAD ARSENATES.

Solution used.	Bean's ortho arsenate. Sol. As <sub>2</sub> O <sub>5</sub> . Per cent. of moist arsenate.	Hemingway's acid arsenate. Sol. As <sub>2</sub> O <sub>5</sub> . Per cent. of moist arsenate.
Distilled water.....	0.073	0.108
Distilled water + CO <sub>2</sub> for two hours.....	0.125	...
0.23 per cent. NaCl, 0.46 per cent. CaCl <sub>2</sub> .....	0.201	0.310
0.10 per cent. Na <sub>2</sub> SO <sub>4</sub> .....	0.106	0.155
Alkali water, 40 grains to gal.....	0.536	1.833

It appears from the above results that both forms of the lead arsenate are more soluble in saline waters than in pure waters. Alkaline carbonate waters especially exert a solvent action on these arsenates and the reaction is much more pronounced in the case of the acid arsenate. This is perhaps due to the fact that lead carbonate is extremely insoluble and that a base with which arsenic forms a soluble salt is present. It is evident that waters containing considerable quantities of alkali carbonates should be avoided in mixing lead arsenate for spraying purposes, as their tendency is to render the arsenic soluble. Tests for lead in the alkaline solutions failed to show its presence therein.

AGRICULTURAL EXPERIMENT STATION,  
CORVALLIS, OREGON.

## THE EFFECT OF GYPSUM ON ALKALI IN SOILS.

By W. F. SUTHERST, PH.D., F.I.C.

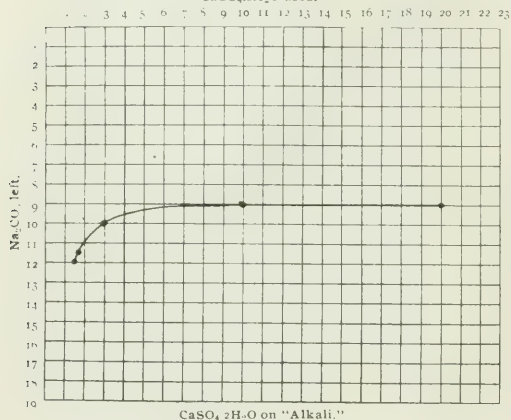
Received April 14, 1910.

One of the remedies suggested for the removal of "alkali" from the soil is to add gypsum, whereby the more detrimental ingredient is supposed to be

<sup>1</sup> Bull. 131, Col. Exp. Sta.

<sup>2</sup> Loc. cit.

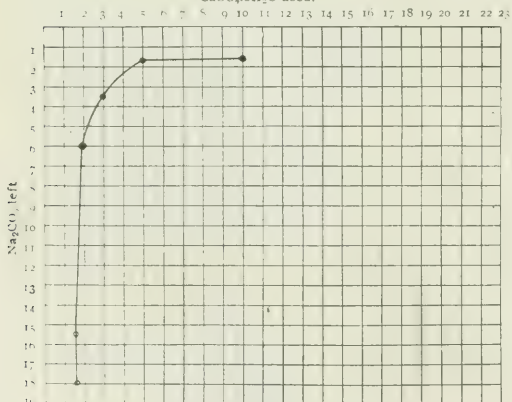
removed. According to the equation, one might expect the whole of the sodium carbonate would be converted into sodium sulfate, especially as the heat of formation of that body is greater than that of

CaSO<sub>4</sub>·2H<sub>2</sub>O used.CaSO<sub>4</sub>·2H<sub>2</sub>O on "Alkali."

sodium carbonate. The action, however, of a sparingly soluble substance is rarely quantitative, and from the following investigation it will be seen that in this instance the reaction is by no means a quantitative one.

The alkali used in these experiments contained 24.45 per cent. sodium carbonate, 22.6 per cent. sodium chlorid, and 40.05 per cent. sodium sulfate.

The method employed consisted in adding increasing amounts of gypsum to one part alkali in 100 parts of water, and as a check, the action of gypsum

CaSO<sub>4</sub>·2H<sub>2</sub>O used.CaSO<sub>4</sub>·2H<sub>2</sub>O on Na<sub>2</sub>CO<sub>3</sub>.

was also tried on pure sodium carbonate. Each mixture was allowed to stand over night and continually agitated, then filtered, and the remaining alkali estimated with normal acid.

The following results were obtained:

Gypsum added.	Exp. I.	Exp. II.
	Na <sub>2</sub> CO <sub>3</sub> left. Per cent.	Na <sub>2</sub> CO <sub>3</sub> left. Per cent.
1.5	.....	12.0
1.75	15.5	11.5
2.0	6.0	.....
3.0	3.5	10.0
5.0	1.75	.....
10.0	1.75	9.0
20.0	.....	9.0

In Exp. I sodium carbonate was used, in II alkali. The limit appears to be reached when 5 per cent. of gypsum was used on soda, and 10 per cent. on alkali. Why a larger amount should be needed in the latter case is probably due to the action of the other salts present. It must be noticed that in II an amount of alkali equal to one part of sodium carbonate was used, so that the two trials could correspond.

That the reaction does not go according to the equation is shown when the theoretical amounts were allowed to react on each other, when it was found that nearly 18 per cent. of the soda in the alkali was unacted upon.

The accompanying diagrams illustrate the results in a clearer way.

## NOTES AND CORRESPONDENCE.

### AN AUTOMATIC PIPETTE.

When a large number of samples of milk are tested for butter-fats by the Babcock method, the work of filling the Babcock bottles consumes considerable time and becomes rather tedious.

With the view of saving time and lessening the work of the operator, the automatic pipette shown in the accompanying illustration was designed.

An ordinary 17.6 cc. milk pipette, the graduation on which is from two to three inches above the shoulder, is cut off at a point slightly above the mark, so that it will hold 17.6 cc. when the finger is placed over the top of the tube. A glass T tube, that will fit loosely over the upper tube of the pipette, is fitted at the lower end with a short piece of rubber tubing so as to make a smoothly sliding joint. The side tube is connected by a length of rubber tubing to a Wolfe bottle. The other neck of the Wolfe bottle is connected to an aspirator by a rubber tube and a glass tube which has been drawn down to a capillary opening to regulate the passage of air.

With the pipette adjusted as shown in the illustration, and the finger placed over the opening of the T tube, milk is drawn into the pipette until it overflows into the T tube. When the T tube is then pushed down, the finger closes the pipette, and the milk may be transferred to the Babcock bottle.

J. BOSLEY THOMAS

### NOTE ON MOISTURE IN VISCOUS PRODUCTS.

In Vol. 1, No. 4, April, 1909, a method was described for "The Rapid Determination of Moisture in Commercial Products of a Viscous or Semi-solid Consistency." The material to be dried was first heated on a steam bath for 30 minutes with

several portions of ethyl alcohol, and then dried to constant weight in a double-walled oven at a temperature of 105° C. Quite some time ago a vacuum oven was substituted for the drying oven previously described and it was found that the time of heating was in many cases shortened, and, what was more important, that oxidation was prevented when drying under high vacuum, so that the same portion on which the moisture was determined could satisfactorily be used for subsequent determinations, where such procedure could not be followed under the ordinary conditions of drying in the presence of air. This has been found to be particularly true in the case of various meats and meat products, cottonseed products and other substances which rapidly oxidize or are otherwise altered at or above boiling water temperature in the presence of air.

ARTHUR LOWENSTEIN.

### LENGTH OF TECHNICAL PAPERS.

MAY 18, 1910.

*Editor Journal of Industrial and Engineering Chemistry.*

DEAR SIR:

In line with the previous notes by Turrentine and Low in the April and May numbers of THIS JOURNAL upon the "Length of a Technical Paper," while I agree with them perfectly inasmuch as they say, I would like to suggest that more careful attention to the following points on part of the author will frequently help to shorten the paper, economize the reader's time and yet enable him to give results enough to make every detail perfectly clear.

1. Be brief in the introduction. We have flowery effusion enough in the literary world.
2. A sketch, a curve or the careful arrangement of the results in tabular form will frequently show at a glance the details of a piece of apparatus or working out of results, which, if expressed in words, would lengthen the article greatly.
3. Give enough results and of sufficiently large variety to enable one to judge for himself as to the author's success with the work in hand.
4. At the end of the article place a summary of the problem and the author's conclusion, telling in a short, concise manner the results of the research and conclusions reached by the author so that the reader will be able to judge at a glance the value of the paper to him.

R. C. BENNER.

### BOOK REVIEWS AND NOTICES.

**Solid Bitumens, their Physical and Chemical Properties and Chemical Analysis, Together with a Treatise on the Chemical Technology of Bituminous Pavements.** By S. F. PECKHAM, A.M., New York and Chicago: The Myron C. Clark Publishing Co., 1909.

Prof. Peckham is one of three or four men living, who are qualified by reason of long, practical acquaintance with the subject, as well as scientific training, to write intelligently on this important class of materials.

By solid bitumens is meant of course what are popularly known as asphalts, but, as Prof. Peckham says in his preface, "the word asphalt has become so hackneyed through misuse that I have avoided its use whenever possible." Using the word bitumen broadly to include naturally occurring products, hydrocarbons or alteration products of the same, whether gaseous, liquid or solid, we have here selected for discussion the class of solid or semi-solid products.

The author devotes some 40 pages to the general question of the origin of bitumens including petroleum, reviewing with the intimate knowledge gained from extended travel and personal inspection the geological teachings on this subject. His view is expressed in the words "no theory that refers the origin of the

bitumen to any physical or chemical action that has prevailed on a cosmic scale can satisfactorily explain the differences that exist in crude bitumens." He believes thoroughly that the bitumens represent the products of the distillation of vegetable and animal tissues brought about by metamorphism. The differences between the purer petroleum of Pennsylvania, with a paraffine base, and the nitrogen and sulphur-containing petroleum of California, with an asphaltic base, are thus explainable.

He gives full credit to the work of Clifford Richardson, which has established the nature of the saturated and unsaturated hydrocarbons of asphalts, and to the extended work of Mabery on the sulphur-containing petroleum of Ohio and California, but does not agree with the views of Dr. H. Köhler and Dr. Geo. Lunge and is inclined to consider the work of the latter especially as superficial.

Coming to the analysis of solid bitumens, he gives a very full account of the methods of both ultimate and proximate analysis with foot-note references to the original publications in most cases. This is followed by a discussion of the methods for the technical analysis of solid bitumens or asphalts, which is historically complete and seems notably fair in its presentations, when we remember that Prof. Peckham has himself taken part in many somewhat spirited controversies over this special question.

The analysis of the allied products, such as street mixtures and surfaces, bituminous paving blocks, bituminous concrete, part in many somewhat spirited controversies over this special wood paving blocks, cements, cement mortars and concrete, etc., are also gone into at considerable length. While much of this is outside of the bitumen classification the subject of cements and concretes is for the paving engineer very closely connected with that of asphalt, and will be acceptable to the technical men searching for information on this line of asphalt utilization.

Lastly the physical properties of solid bitumens such as specific gravity, softening point, ductility and resistance to penetration are taken up and the methods for experimental determination of these qualities at present in use are described.

The work shows, as said at the beginning, evidence of having been written by one thoroughly conversant with the subject. Perhaps because of this fact more of the controversial side of the subject has appeared and less descriptive accounts of the many and varied forms of solid bitumens found in various countries but as I have said the author has always been fair in presenting all sides of the questions discussed.

The work is well printed and made, but a number of typographical errors have escaped the proof-reader and should be corrected in another edition.

SAM. P. SADDLER.

### SCIENTIFIC AND INDUSTRIAL SOCIETIES.

#### THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

Second semi-annual meeting, June 22-24, 1910.

Sessions held at Hotel Clifton, Niagara Falls, Canada.

Office of the Secretary, Polytechnic Institute, Brooklyn, N. Y.

WEDNESDAY, JUNE 22, 1910.

9.30 A.M. Meeting at Hotel Clifton.

Address of Welcome.

Business Session.

Reports of Officers and Council.

Reports of Committees.

11 A.M. Reading of Papers:

"Changes in Industrial Chemistry Caused by Electricity,"

Edward R. Taylor.

"Notes on the Corrosion of Iron and Steel and its Prevention," G. W. Thompson.



"Vacuum Distilling Apparatus," Philip B. Sadtler.

12.30 P.M. Luncheon.

1.30 P.M. Excursions.

Ontario Power Co.

Alternative.

International Paper Co. (Paper and Pulp Mill.)

7.30 P.M. Meeting at Hotel Clifton.

Address of President McKenna. "The Study of Materials as an Element in a Course of Chemical Engineering."

Report of the Committee on Chemical Engineering Education," F. W. Frerichs.

"A New Product for Use in the Arts," F. G. Wiechmann.

THURSDAY, JUNE 23, 1910.

Excursions:

Lackawanna Steel Co.

Alternatives.

H. W. Dopp Co's. Plant.

Linde Liquid Air Plant.

Buffalo Foundry and Machine Co.

Regarding the train to be taken to reach the plant of the Lackawanna Steel Company, announcement will be made at the meeting. The plant will probably be reached about 10 A.M.

2 P.M. Excursions:

Larkin Soap Co.

7 P.M. Dinner.

Subscription dinner at Hotel Clifton (\$3.00). (The guests of Hotel Clifton will receive credit on this item.)

FRIDAY, JUNE 24, 1910.

9.30 A.M. Meeting at Hotel Clifton.

Reading of Papers:

"Chemical Industries of Canada," J. A. DeCew.

"The Manufacture and Industrial Applications of Ozone," Oscar Linder.

"Problems in Chemical Industry," J. T. Baker.

"Arrangement of Filter Presses for Bleaching Oils with Fuller's Earth," David Wesson.

"Commercial Manipulation of Refractory Elements for Incandescent Lamp Purposes," Ralph E. Myers.

12 M. Luncheon.

1 P.M. Excursions:

Acheson Graphite Co.

Hooker Electrochemical Co.

7.30 P.M. Meeting at Hotel Clifton.

Reading of Papers:

"Underground Waters for Manufacturing Purposes," W. M. Booth.

"Loss in Coal Due to Storage," A. Bement.

"Nitric and Mixed Acids," Schuyler Frazier.

"Plant Design," W. M. Grosvenor.

9 P.M. Business Meeting. Final Session.

SATURDAY, JUNE 25, 1910.

Excursions:

Wickwire Steel Co.

Niagara Falls Power Co.

Carborundum Works.

#### AMERICAN SOCIETY FOR TESTING MATERIALS.

Affiliated with the International Association for Testing Materials.

Thirteenth Annual Meeting Atlantic City, N. J., June 28th, July 2, 1910. Headquarters, The Hotel Traymore.

#### PROGRAM.

##### First Session.

TUESDAY, JUNE 28TH, 3 P.M.

1. Minutes of the Twelfth Annual Meeting.
2. Annual Report of the Executive Committee.

3. Report of Committee A-3: "On Standard Specifications for Cast Iron and Finished Castings," Walter Wood, *Chairman*.
4. "Tests of Cast-Iron Arbitration Test Bars," C. D. Mathews.
5. "Some Recent Tests of Cast Iron," A. E. Outerbridge, Jr.
6. "Notes on the Annealing of Steel Castings," Albert Sauveur.
7. "Untruly and Unevenly Chilled Car Wheels," T. D. West.
8. Report of Committee E-1: "On Standard Methods of Testing," Gaetano Lanza, *Chairman*.
9. Report of Committee B-1: "On Standard Specifications for Hard-Drawn Copper Wire," J. A. Capp, *Chairman*.
10. "The Forest Products Laboratory, its Purpose and Work," McGarvey Cline.
11. Election of Officers.
12. Miscellaneous Business.

##### Second Session.

TUESDAY, JUNE 28TH, 8 P.M.

13. "The Closing of Blowholes in Steel Ingots," Henry M. Howe.
14. "Measured Strains in a Steam Boiler under Hydrostatic Tests," James E. Howard.
15. "Copper Clad Steel, its Metallurgy and Properties," Wirt Tassin.
16. "Tests on Steel and Wrought-Iron Beams," H. F. Moore.
17. "Strength of Steel from I Beams," E. L. Hancock.

##### Third Session.

WEDNESDAY, JUNE 29TH, 10 A.M.

##### On Steel.

18. Report of Committee A-1: "On Standard Specifications for Steel," William R. Webster, *Chairman*.
19. "Low-Carbon Streaks in Open-Hearth Rails," M. H. Wickhorst.
20. "Elongation and Ductility Tests in Rail Sections under the Manufacturers' Standard Drop-Testing Machine," P. H. Dudley.
21. "The Influence of Titanium on Segregation in Bessemer-Rail Steel," G. B. Waterhouse.
22. "Cupro-Nickel Steel," G. H. Clamer.
23. "Test of a Structural Steel Plate Partly Fused by Short-Circuited Electric Current," A. W. Carpenter.
24. Report of Committee A-8: "On Standard Specifications for Cold-Drawn Steel," C. E. Skinner, *Chairman*.
25. "Further Notes on the Heat Treatment of Steel," Wm. Campbell.

The afternoon of Wednesday, June 29th, will be reserved for sea-bathing, sailing, fishing, golf and general recreation.

##### Memorial Session.

WEDNESDAY, JUNE 29TH, 8 P.M.

In honor of the memory of Dr. Charles B. Dudley, late President of the International Association for Testing Materials and of the American Society for Testing Materials.

*The Life and Life-Work of Charles B. Dudley, 1842-1909.*

Mr. R. W. Lesley, Vice-President of the Society, will say an opening word on behalf of the Executive Committee. "As a Railroad Man," Theodore N. Ely; "As a Chemist," Edgar F. Smith; "As a Metallurgist," Henry M. Howe; "As a Mentor," B. W. Dunn; "As a Citizen," W. H. Schwartz; "A Personal Tribute," R. W. Hunt.

##### Fifth Session.

THURSDAY, JUNE 30TH, 10 A.M.

##### On Cement and Concrete.

26. Report of Committee C-1: "On Standard Specifications for Cement," George F. Swain, *Chairman*.

27. "Aluminates: Their Properties and Possibilities in Cement Manufacture," Henry S. Spackman.
28. "The Effect of Sodium Silicate Mixed with or Applied to Concrete," Albert Moyer.
29. "Comparative Tests of Lime Mortar, both in Tension and Compression; Hydrated Lime and Sand, Lump Lime and Sand, and Cement Lime and Sand," E. W. Lazell.
30. "Tests on Reinforced Concrete Columns Subjected to Repeated and Eccentric Loads," M. O. Withey.
31. "The Distribution of Stress in Reinforced Concrete Beams, Including a Comparative Study of Plain Concrete in Tension and Compression," A. T. Goldbeck.
32. "A Sand Specification and its Specific Application," W. A. Aiken.

*Sixth Session.*

THURSDAY, JUNE 30TH, 3 P.M.

*On Preservative Coatings and Oils.*

33. Report of Committee D-1: "On Preservative Coatings for Structural Materials," S. S. Voorhees, *Chairman*.
34. Report of Committee A-5: "On the Corrosion of Iron and Steel," A. S. Cushman, *Chairman*.
35. "A Method for Testing the Protective Power of Paints when Applied to Iron and Steel," W. H. Walker and M. T. Jones, Jr.
36. "Another Solubility Test on Protective Coatings," G. W. Thompson.
37. "Vermilion Paint for Railway Signals—Results of an Investigation," Robert Job.
38. "The Painting of Cement and Concrete Structures," Charles MacNichol.
39. "Classification of Fine Particles According to Size," G. W. Thompson.
40. Report of Committee D-2: "On Standard Tests for Lubricants," A. H. Gill, *Chairman*.
41. Report of Committee D-3: "On Standard Methods of Analysis of Fats and Oils," C. N. Forrest, *Chairman*.

*The evening of Thursday, June 30th, will be reserved for an Engineering Smoker.*

*Seventh Session.*

FRIDAY, JULY 1ST, 10 A.M.

*On Testing Machines and Apparatus.*

42. "The 600,000-lb. Testing Machine of the University of Wisconsin," H. F. Moore and M. O. Withey.
43. "The Scleroscope," A. F. Shore.
- This paper will be followed by a general discussion on "Tests of Metals for Hardness," to be opened by Mr. A. F. Shore, Mr. Bradley Stoughton and Mr. A. S. Sauveur.
44. "Some Testing-Laboratory Accessories," J. Madison Porter.
45. "Brinell Ball-Test Applied to Wood," W. K. Hatt.
46. "Apparatus for Repeated Loads on Concrete Cylinders and a Typical Result," H. C. Berry.
47. "An Autographic Rubber-Testing Machine," T. Y. Olsen.
48. "The Work of the Structural Materials Testing Laboratories during the Past Year," R. L. Humphrey.

An exhibit of photographs and drawings of testing apparatus, contributed by the Testing Laboratory of the Engineering College of the University of Wisconsin, will be displayed at this session.

*Eighth Session.*

FRIDAY, JULY 1ST, 3 P.M.

49. "The Determination of Soluble Bitumen," Prévost Hubbard and C. S. Reeve.

The discussion of this paper will be opened by Mr. S. R. Church, Mr. A. W. Dow, Mr. W. H. Fulweiler, Mr. Clifford Richardson and Mr. Albert Sommer.

50. "Improved Instruments for the Physical Testing of Bituminous Materials," Herbert Abraham.
51. "Necessary Reforms in Specifications for Petroleum Products," Albert Sommer.
52. "A New Machine for Testing Pitch," T. Y. Olsen.
53. Report of Committee D-8: "On Waterproofing Materials," W. A. Aiken, *Chairman*.
54. Report of Committee D-9: "On Standard Tests of Insulating Materials," C. E. Skinner, *Chairman*.
55. Report of Committee D-5: "On Standard Specifications for Coal," J. A. Holmes, *Chairman*.
56. "Fuel Investigations, U. S. Geological Survey; Progress during the Year Ending June 30, 1910," J. A. Holmes.

*The evening of Friday, July 1st, will be reserved for recreation.*

*Ninth Session.*

SATURDAY, JULY 2ND, 10 A.M.

57. Report of Committee C-3: "On Standard Specifications for Paving and Building Brick," L. W. Page, *Chairman*.
58. Report of Committee D-4: "On Standard Tests for Road Materials," L. W. Page, *Chairman*.
59. Report of Committee C-4: "On Standard Specifications for Vitrified Clay and Cement Sewer Pipe," Rudolph Hering, *Chairman*.
60. Report of Committee D-7: "On Standard Specifications for the Grading of Structural Timber," H. von Schrenk, *Chairman*.
61. Report of Committee A-6: "On the Magnetic Testing of Iron and Steel," J. W. Esterline, *Chairman*.
62. "A Comparison of Magnetic Permeameters," Charles W. Burrows.
63. "The Exponential Law of Endurance Tests," O. H. Basquin.
64. Miscellaneous Business.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**956,734. Process of Manufacturing Methane or of Mixtures of Methane and Hydrogen.** PAUL SABATIER, Toulouse, France. May 3, 1910.

This invention relates to a process for the manufacture of methane or of mixtures of methane and hydrogen by passing water gas over heated nickel.

The invention is characterized by the fact that the water gas used has a constant composition which is obtained by observing a constant temperature in the apparatus for producing such gas. The water gas is subsequently deprived of carbonic acid in two stages, it is treated first of all with sodium carbonate in a known manner and is afterward passed through a dilute solution of sodium hydrate. In this double operation for removing the carbonic acid, the gas becomes sufficiently moist so that it can be passed on to the nickel without adding water vapor. No carbon is deposited in this process; a mixture of gases is obtained that always contains the same proportions of methane and hydrogen.

In the accompanying illustration, an apparatus is shown, by way of example suitable for the purpose of carrying out the process.

The water gas is manufactured in apparatus A, with bent tubes or straight horizontal or inclined tubes *b* as shown in the illustration by way of an example. The superheated steam produced in the generator *c* passes through *d* to the coke (anthra-

cite, wood, charcoal), the latter being heated by a furnace, B, heated with coal, or preferably by the gases produced by a Siemens or an analogous generator. A pyrometer, C, with constant indications such as Le Chatelier's thermoelectric pyrometer will allow of the average temperature in the tubes *b* being determined. The pyrometer is fixed at the angle of the bent tubes or in the middle of the straight tubes. The composition of the water gas depends: (1) On the temperature of the coal. (2) On the nature of the coal. The higher the temperature the smaller the proportion of carbonic acid. The amount of carbonic acid contained in the gases can easily be determined. If this amount is about 20 per cent. the gas is just in condition for the manufacture of pure methane. A reading is taken with the pyrometer and it is sufficient to keep the temperature at the

and methane are to be prepared simultaneously the retorts of the gas factory may be used for generating water gas by introducing water vapor before the glowing coal is removed, such water vapor being afterward transformed into methane.

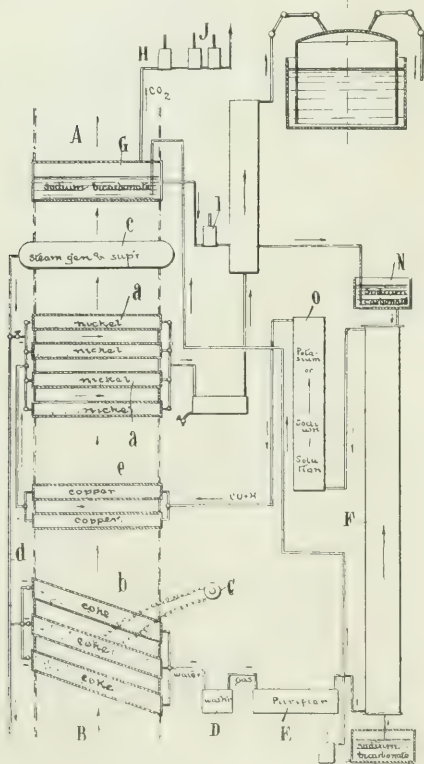
The gas to be deprived of carbonic acid is passed in at the bottom of a vertical column, F, in which a sodium carbonate flows down. The liquid that runs out contains of course sodium bicarbonate. The same is passed into boilers, G, that are heated with the hot gases that come out of the water gas furnace. In these boilers carbonic acid gas is given off. The production of carbonic acid gas by the decomposition of the bicarbonate may be facilitated by aspirating with a pump, H. The liquid that finally contains the neutral carbonate only is brought back to the column F by suitable pumps, I, and the whole operation is started over again. The carbonic acid gas cannot, however, be completely removed in this manner owing to high tension of the dissociation of the bicarbonate, especially at the temperatures that supervene in summer. The removal of the carbonic acid is completed by passing the gas through a small column, O, in which a dilute solution of potassium or sodium hydrate is made to circulate or by passing the gas through chambers in which a layer of slaked lime is spread out. If potassium hydrate is used or sodium hydrate this material is recuperated from time to time by heating the same with lime. In the case of potassium the resulting carbonate of lime retains a little potassium hydrate and may subsequently be made use of in agriculture as a fertilizer. The carbonic acid that escapes from the boilers G may be liquefied at J by compression in a known manner and may be placed on the market as liquid carbonic acid.

The practical execution of this reaction depends on the following conditions: (1) The initial cleaning of the gas. (2) The arrangement of the apparatus. (3) The preparation of the nickel. (4) The way of conducting the operation.

(1) The gas deprived of carbon dioxide at O consists of a mixture of carbon monoxid and hydrogen. It must be free from traces of sulfur compounds that it may contain and for this purpose the gas is made to pass through tubes *e* containing copper in the shape of turnings or of a fine powder. These tubes are built into water gas furnace, A B, above the carbon tubes and must be maintained at a temperature between 500° and 600° C. The copper heated to dark red withholds any impurities that might deteriorate the nickel. After long use the copper becomes partly transformed into copper sulfid and must be renewed. The copper sulfid may be submitted to a roasting process so as to obtain copper oxid, and the latter may be restored to metallic copper by treating the oxid with the gas to be purified.

(2) The apparatus for the reaction with nickel consists of horizontal metallic flattened tubes, *a*, into which flat receptacles containing nickel are introduced. These tubes are arranged in series in furnaces that are heated by the hot gases of the water gas furnace. The temperature may be controlled by thermometers or by means of pyrometers that indicate continuously. Vertical cylinders may likewise be used that are supplied with horizontal plates on which the nickel is placed, the gases being made to circle around these plates. The hot gases of the water gas furnace are made to heat successively after heating the carbon tubes *b*, the tubes *e* provided with copper, the tubes *a* or the horizontal plates for producing hydrogen and finally the boilers G for decomposing the sodium bicarbonate.

(3) The nickel producing the catalytic reaction must be in a powdered condition and is obtained by reducing the nickel oxid to be had in the trade. The reduction may be effected in the same apparatus that is used for carrying out the present invention. The oxid is reduced by applying the mixture of carbon monoxid and hydrogen that issues from the copper



degree it has attained. If the proportion of carbonic acid gas is lower than 20 per cent., the furnace is too hot and the heating must be regulated so as to attain the proportion required. If a mixture of methane and hydrogen is to be prepared the temperature must be lowered until the pyrometer shows a temperature that corresponds to the proper proportion of carbonic acid gas. In a furnace fed with light coke the proportion of 20 per cent. of carbonic acid corresponds to 970° read off the pyrometer. At 780° 24 per cent. of carbonic acid is obtained and 12 per cent. of carbon monoxid. This mixture ought to yield about 33 per cent. methane and 67 per cent. hydrogen. The water gas prepared in this manner is washed at D and cleaned at E with a Laming mixture before being deprived of carbonic acid gas. When ordinary gas for lighting purposes



tubes. The reduction ought to be effected between 350 and 450° C.

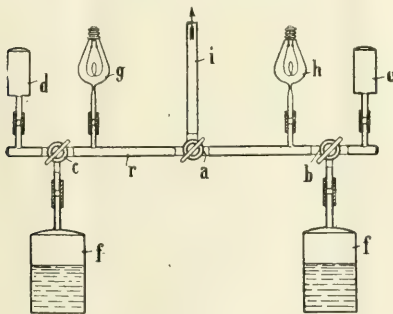
(4) The tubes (or flat cylinders) for the nickel are grouped in several series that are independent of one another, so that one series may be emptied, filled again and reduced without interrupting the whole operation.

(5) The reaction with nickel is effected preferably at 350° C., but the temperature may vary between 300 and 450° C. without involving any serious disadvantage. As the gases are moist when they reach the nickel and the reaction is accomplished by a considerable production of water, the permanent formation of carbon on the nickel according to the reaction  $\text{CO} = \text{C} + \text{CO}_2$  does not take place. This may easily be verified by examining the gas after leaving the apparatus. The same will be found to contain no appreciable quantities of carbonic acid.

**958,652. Method of Regenerating Carbon-filament Electric Incandescent Lamps.** ERNST AUGUST KRUGER, of Seehausen, Altmark, Germany. May 17, 1910.

The reason of carbon filament lamps becoming black is that in the course of their life very fine particles of carbon are thrown off from the carbon filament and are deposited on the inner wall of the glass bulb. Owing to the glass bulb being blackened the light radiated from the lamp is diminished, but simultaneously, owing to the particles of carbon being thrown off from the carbon filaments, the latter are weakened so that when the lamp is continued to be used the danger of the filament burning through at its weakest place always becomes greater.

As long as the carbon filament in a lamp is not broken, the lamp can be regenerated according to the present method. For this purpose the blackened lamp is first opened at its point so that air can enter into the bulb; simultaneously for the purpose of subsequently evacuating the bulb, a tube is attached by fusion to the point of the bulb. The glass bulb is now or subsequently highly heated by means of an open flame so that the black coating of the glass wall burns away. The lamp is now prepared for the execution of the regenerating method proper. The glass receptacle is evacuated and a suit-



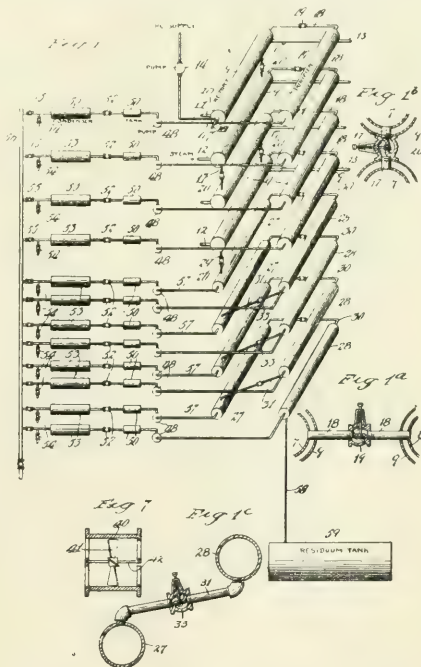
able hydrocarbon is introduced into the bulb. If an electric current of suitable strength is now sent through the carbon filament so that the latter is caused to glow, the hydrocarbon is decomposed and carbon is deposited, as is well-known from the preparation of the carbon filament, in a very dense form on the filament, namely the filament is flashed. The flashing is continued until the filament has acquired a uniform strength. When this is so, the lamp is evacuated again and sealed. It is then ready for use and is stated to be exactly as good as a lamp having a perfectly new carbon filament. The method can be repeated optionally frequently in the case of every lamp when the glass bulb has become blackened again.

In carrying out the process at the beginning the three-way cock *a* is so turned that a lamp, *g*, and receiver, *d*, for example are evacuated. Then by turning the cock *a* the lamp *g* is separated from the pump and the lamp *h* is evacuated. By turning the cock *c* a definite quantity of a suitable heavy hydrocarbon is now sucked from the storage receptacle *f* into the receiver *d*. Hereupon the storage receptacle *f* is cut off again by turning the cock *c* and the receiver *d* is connected with the lamp *g*; the hydrocarbon necessary for flashing the filament consequently enters into the lamp bulb where it is decomposed when current traverses the carbon filament. A similar series of operations is performed for treating the lamp *h*. For removing the black coating from the inner wall of the lamp it is preferable to heat the bulb to a high temperature by means of an open flame after the filament has been flashed. The preliminary receivers *d* and *e* are arranged for the purpose of preventing the hydrocarbon flowing into the lamps too violently, since the carbon filaments might otherwise be destroyed. It is to be understood that the hydrocarbon may be placed in the receivers *d* and *e* from the very first.

**958,820. Process for the Treatment of Oils.** JOSEPH H. PARKER, of Los Angeles, California. May 24, 1910.

This invention relates to the treatment of hydrocarbon oils for the production of one or more oil products therefrom, said oil products being, in general, of less density and viscosity than the original oil.

The patentee claims to have discovered that in the distillation of oils, the maximum quantity of liquid hydrocarbons, is obtained by distillation under high pressure and low temperature,



with subsequent rapid condensation, and an important object of the present invention is to utilize the advantages of such a mode of operation.

The process consists essentially in forcing oil, together with

steam, at high velocity into a chamber which is maintained under pressure, causing the oil while in said chamber to be broken up and to be distributed over an extended surface to generate a vapor, withdrawing from time to time a portion of the vapor so generated from said chamber, withdrawing the unvaporized portion of the oil from said chamber, and passing it into a second chamber, repeating such operation in said second chamber, and continuing this operation in a series of steps, the oil being divided at each step into a vaporized portion and an unvaporized portion, and the vaporized portion being withdrawn suddenly and in successive intermittent discharges from the respective chambers.

An important feature of the process is the dependence on mechanical action of division and extension of the oil over surfaces for the formation of vapor therefrom for dividing the oil into its component parts, rather than on the chemical effect of heat in breaking up the oil or changing its chemical combinations.

The apparatus for carrying out the process is shown in the accompanying illustration and comprises retort means for subdividing the oil and exposing it over an extended surface at progressively higher temperatures, to generate successive portions of vapor therefrom, pulverizing or atomizing means for mechanically breaking up and mixing the vaporous products, means for drawing off vaporized product from the retort means and compressing the same, automatically operating means for causing such withdrawal of the vaporized product to be intermittent and at determinate pressures, means for compressing the vapors, means for condensing the compressed product, and means for delivering the condensed liquids separately or blended, as may be required.

950,237. Process of Converting Starch into Derivatives, Dextrin, Dextrose, Etc. SAMUEL MORRIS LILLIE, of Philadelphia, Pa. May 24, 1910.

The purpose of this invention is to provide a continuous process of converting starch by means of heat, acid and water into derivatives dextrin, dextrose, etc., and to obtain a practically uniform conversion, a constant draw of steam from the

boilers, and other advantages incidental to a continuous process.

The process of treating the starch consists in mixing the starch with water and acid to form a mixture of the desired mobility and acidity in quantities sufficient to supply requirements; in forcing the said mixture of starch, water and acid continuously and at a uniform rate of flow, corresponding to the quantity of product wanted, through suitable heating devices and heating it therein under pressure to the desired converting temperature, say  $280^{\circ}$  F., making this heating period so brief that the starch mixture on leaving it will have suffered only a partial conversion; in delivering this but only partially converted heated mixture with an even distribution over the cross section of a column of the mixture, to which no more heat is added, moving uniformly through a containing vessel in which vessel the pressure is maintained not less than that corresponding to the converting temperature to which the mixture has been raised; in withdrawing from the end of the column the mixture at the same rate at which it is being delivered to the column at the opposite end, *i. e.*, the uniform rate necessary to produce the desired quantity of product in a given time; in varying the length or depth of the said column of mixture to vary the length of time the liquors shall be subject to the converting temperature and thereby vary the degree of conversion; and finally in neutralizing the acid in the mixture by means of a suitable reagent, approximately at the time it leaves the end of the column, or just prior to this.

## INDUSTRIAL AND TRADE NOTES.

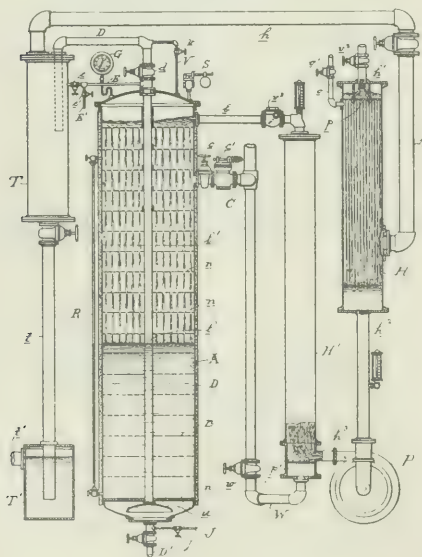
*Potassium Cyanid Manufacture.*—Writing from Prague, Consul Joseph I. Brittain says that a large plant recently constructed in Austria for making potassium cyanid from thick molasses, a by-product from beet-sugar factories, is attracting attention from other countries where similar manufacturing establishments are contemplated. The consul's description of the process will therefore be of value:

The only factories where potassium cyanid is made from a by-product of sugar beets are two in Germany and one at Kolin, 40 miles east of Prague, Bohemia. The molasses by-product is sold to factories manufacturing alcohol, which by fermentation and distillation produce a first quality 97.7 per cent. pure alcohol for medicinal and chemical purposes, and a second quality denatured for fuel and light. The refined wholesales at \$12.27 and the denatured at \$9.13 to \$9.54 for 26.41 gallons. The former pays an internal-revenue tax of \$18.27 per 26.41 gallons.

After making the alcohol there remains a still thicker and darker colored molasses, resembling pine tar in appearance. This residue is sent from the various alcohol factories in tank cars and barrels to Kolin where, after subjected to steam heat, it flows into long metal troughs and to retorts where it is burned for several hours, until the gas escapes into pipes. The material then passes through an extended system of pipes, undergoing various processes until it reaches the place where it is mixed with lye, when the potassium cyanid is formed, after which the moisture is extracted by centrifugal force. The powder is then conveyed to another room, where it is hydraulically pressed into cakes and packed into boxes for shipment. The output of the Kolin factory is about 240,000 pounds a month, and is sold to gold and silver mining companies in South Africa.

The building where the gas is generated is 260 by 68 feet, and contains eight furnaces, with 56 retorts for burning molasses and generating gas. The main building containing the pipes and machinery, as well as the centrifugal machinery, is 195 by 45 feet. The machinery and boiler rooms are 67 by 65 feet, and 40 by 67 feet, respectively.

(To be Continued.)



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## ORIGINAL PAPERS.

### A NEW GAS CALORIMETER.

By S. W. FARR.

Received June 27, 1910

Undoubtedly the calorimetry of gases will receive more attention in the future than it has in the past, owing to the fact that both for lighting and power the heat content is of more importance than the candle value; and, while there is a certain relation between the two, it is not sufficiently consistent to permit of the heat units being deduced from the indicated candle power. That there is to be a transfer of standards is indicated by the recent action of the Railroad Commission of Wisconsin<sup>1</sup> and the careful study of the matter now being carried on by the Gas Commissioners of New York State,<sup>2</sup> and also by a special committee appointed by the American Gas Institute on the Calorimetry of Gases.<sup>3</sup>

The importance of the subject, therefore, being in a fair way to receive recognition, it is well at this stage to scrutinize closely the essential conditions necessary for the accurate measurement of the heat

value of a combustible gas. In the first place, the conditions are essentially different from the usual methods available for the calorimetry of coal, in that the products of combustion being gases, the absorption of heat involves the principle of convection rather than that of conduction; that is to say, the passage of heated gases over absorbing surfaces is a necessary condition where combustion of gases is involved. If, now, we will add to this fundamental conception the fact that the composition of the majority of combustible gases is of such a nature as to yield upon burning a certain amount of water which condenses, we have a condition resembling that of a wet bulb thermometer over which the currents of air are passing and which affect by the process of vaporization the temperature of the water of the interior of the system. That the exterior parts of such an apparatus are insulated and that the absorbing surfaces are on the interior and hidden from view does not alter the case. If these bare surfaces with the currents of air passing over them were placed on the outside and kept moistened, we would see, though in an exaggerated manner perhaps, the actual condition by which we are attempting to measure heat imparted by the burning of a gas which at the same time carries with it a large excess of circulating air. To just what extent there is thus brought about a modification in the actual heat discharged, it is not easy to determine. An estimate may be made of the relative quantity of air which accompanies a certain metered volume of gas and the humidity of such air taken upon entering and assumed to be saturated when discharged. Coste<sup>1</sup> has made such calculations based upon certain conditions which would seem to indicate a loss of less than 1/10 per cent. and is, therefore, negligible. There are, however, too many uncertainties or variables, such as relative humidities and ratio of air volume to gas, to admit of thus finally disposing of the matter. The loss also due to direct radiation must be considerable, since the outflowing water where the temperature is taken exceeds the room temperature by from 10° to 20°.

In order to directly indicate the error due to these conditions, a flow-type calorimeter was installed to operate upon a standard gas of known value. The procedure was as follows: pure hydrogen generated on the principle of the Parsons generator<sup>2</sup> for sul-

<sup>1</sup> Report, Wisconsin Railroad Commission, No. 1, 21, July 1908, pp. 19-33.

<sup>2</sup> N. Y. Public Service Commission, 2nd District, 3rd Annual Report, 1909, p. 19.

<sup>3</sup> *Proc. Am. Gas. Inst.*, 1908, p. 287.

<sup>1</sup> *J. Soc. Chem. Ind.*, 28, 1233.

<sup>2</sup> *J. A. C. S.*, 25, 231.



phuretted hydrogen was used, a continuous supply being thus secured in such quantity as to operate a Junker calorimeter at standard speed and under prescribed conditions. The precautions for accuracy may be briefly outlined as follows: after washing the gas in a dilute alkaline solution it was passed through a wet meter and pressure regulator. In standardizing the meter it was found to be not only in error approximately 2 per cent. to 4 per cent., but the error was variable and for no assignable cause. No suitable device was present on the meter for establishing a water-level—the automatic drain could be made to yield a water-level varying by over 100 cc. After extended and quite elaborate efforts to make this meter read correctly or with a known and determinable factor of error, it was abandoned as impossible. A meter from the American Meter Company was substituted, with satisfactory results in this regard. It is true, however, that a variation in speed causes a variation from the exact or standard volume, but in carrying on the experiments a speed was adopted which more nearly represented the correct reading for the volume of gas passing through the meter; namely,  $6\frac{1}{2}$  feet per hour. A series of experiments to determine the best type of burner resulted in the adoption of an acetylene burner known as Bray's "Elta," or rather two  $1\frac{1}{4}$  foot burners of this type placed side by side and mounted in the ends of a glass Y, the branches softened and brought close together so as to be properly adjustable in the combustion chamber. The type of burner used as well as the mounting on a glass stem insured the minimum of conduction of heat downward, and the type of flame insured a complete combustion at all speeds.

According to the specification of the Committee on Gas Calorimetry for the American Gas Institute, the ideal conditions and those which would seem to be theoretically necessary require that the exhaust gases from the instrument and the room temperature, as well as the entering gas, be as nearly as possible the same. A series of tests shown in Table I was made in which these conditions were maintained, giving a heat value per cubic foot of hydrogen, calculated to  $60^\circ$  and  $30^\circ$  of mercury, as indicated in Table I.

If we adopt Thomsen's value for the conditions indicated, which would be 325 B. t. u., we see that there is present a constant error of 13 to 15 B. t. u., or approximately 4.5 per cent., referring to 325 as a basis.

If, now, we vary the conditions as to the temperature of the exit gases, we will be proceeding on the theory that a compensation is due the system for the heat carried away by the evaporation of water. This will be accomplished by having the exit gases lower than the temperature of the room. By this

means a point could be reached where the heat absorbed by the system would compensate for the heat carried away by the circulating atmosphere.

TABLE I.

Gas temp. Degrees F.	Room temp. Degrees F.	Exhaust temp. Degrees F.	Heat value. B. t. u./cu. ft.
79.0	80.3	80.0	311.1
79.0	79.0	79.0	311.4
82.0	82.0	82.0	310.0
83.0	84.0	84.0	311.5
83.0	84.0	84.0	311.7
83.0	84.0	84.0	312.0
83.0	82.5	82.5	310.4
83.0	82.5	82.5	312.1
83.5	83.0	84.0	310.9
83.5	83.0	84.0	310.4
81.0	82.0	82.0	309.8
81.5	82.0	82.0	310.2
78.0	77.5	78.0	310.7
78.0	77.5	78.0	311.5
78.0	80.0	80.0	311.1
78.0	81.0	80.0	309.9
77.0	78.0	78.0	309.3
77.0	78.0	78.0	310.7
77.0	78.0	78.0	311.5
76.5	77.0	76.5	311.5
76.5	77.0	76.5	311.1

The following table, II, not only establishes the fact of such compensation, but arrives at the factor of error directly and not by calculation from uncertain premises. By reference to the table it will be seen that with the temperature of the exhaust gases  $5.5^\circ$  below that of the room, the indicated heat value comes up to  $325^\circ$ , the accepted value for hydrogen. By examination of the entire series which ranges from a temperature of  $+4^\circ$  to  $-10^\circ$  and plotting a curve from the points thus indicated as ordinates

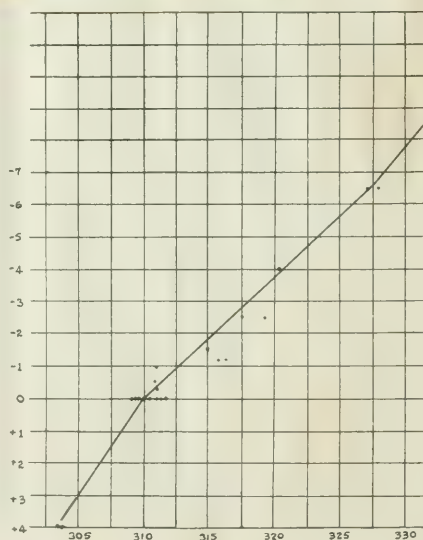


FIG. 1.

with the B. t. u. derived from each test at the designated temperature as abscissas, we have a very con-

sistent showing as to the effect of the variations in temperature of the outlet gases:

TABLE II.

Gas temp. Degrees F.	Room temp. Degrees F.	Exhaust temp. Degrees F.	Heat value B. t. u./cu. ft.
82.0	83.5	82.0	315.0
83.0	83.0	79.0	320.6
83.0	83.0	72.5	336.1
77.0	79.0	78.0	315.9
77.0	79.0	78.0	316.6
78.0	76.5	72.5	320.6
82.0	82.0	82.0	310.0
83.0	82.0	72.0	335.6
83.0	82.0	72.0	334.9
80.0	78.0	71.5	327.4
80.0	78.0	71.5	328.1
80.0	78.0	75.5	317.6
80.0	78.0	75.5	319.4
81.0	82.0	82.0	309.4
86.0	86.0	90.0	303.4
86.0	86.0	90.0	303.5

From this data it would appear that under the conditions prescribed by the Committee of the American Gas Institute the Junker calorimeter is in error, aside from errors of the meter, from 13 to 15 units in 325, or approximately  $4\frac{1}{4}$  per cent. Doubtless the entire explanation for this does not reside in the matter of relative humidity of the air but involves also, as already indicated, a loss due to radiation. It is difficult, if not impossible, to measure this latter loss, but from the curve it seems possible to arrive at an average of all errors though they may vary appreciably under the different conditions of operation as to temperatures, humidity, etc.

If we wish to compare this indicated error with conditions of humidity, evaporation, etc., which would result in an equivalent variation from the standard, we would need approximately the following data:

10 cu. ft. of air to 1 cu. ft. of gas.	
Room temperature.....	77° F.
Relative humidity of air.....	20 per cent.

Then, 10 cu. ft. saturated air at 77° F. would carry 6.5 grams of water. A vaporization, therefore, of, say, 5 grams of water at 2.4 B. t. u. per gram shows a loss of 12 B. t. u. per cu. ft. of gas burned, or a little less than 4 per cent. A part of the variation undoubtedly should be ascribed to radiation, but the above hypothetical calculation alone accounts for the major part of the error. It is, moreover, entirely within the range of working conditions and shows a result in marked contrast to the calculation by Coste above referred to. In any event, if a less error is due to heat of vaporization, then more should be ascribed to radiation since the above experimental method of arriving at the sum of the variables would seem to be preferable to any calculation based on uncertain premises.

In the new type of instrument here proposed, two parallel systems are so arranged that equal volumes of gases may be taken and placed under equivalent conditions as to temperature and pressure, being submerged in the same vessel of water and

having the same water head for pressure. These gas volumes are arranged with burners placed under equivalent amounts of water, with conduits and stirrers devised so as to extract all of the heat. The rise in temperature is indicated on thermometers graduated to tenths, readable by means of the lenses to hundredths of a degree Fahrenheit. It will be seen that the rise in temperature of the two systems will be in proportion to their heat values. If, therefore, one of the systems employed be a standard gas, such as hydrogen or acetylene, and the value of that gas be taken at standard conditions, such as 60° F. and 30" of mercury, the standard chosen will be to the heat value of the unknown gas, at the same condition as to temperature and pressure, as the ratio of the indicated rise in temperature of the two thermometers. The details of the apparatus are carried out with reference to this principle. The stirring of the water is effected by a small motor with a common belt actuating the two pulleys, with turbines arranged on the interior of the heaters.

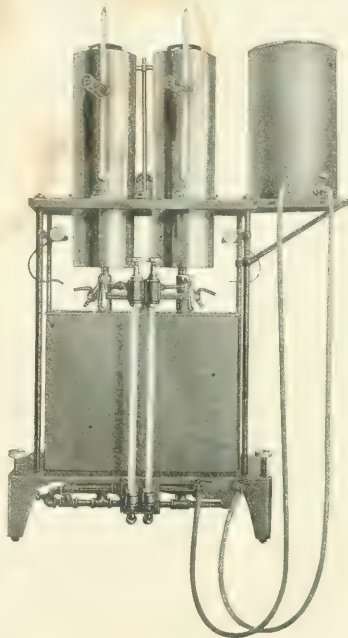


Fig. 2

The heaters are arranged with automatic overflows at the rear, which can be adjusted to measure exact equivalents of water. Provision is made for measuring the volumes of the gases with accuracy by reducing the area of the containing vessels above and below so that the starting and stopping point may be accurately indicated on the glass gauges in front. The gas-holders are cylinders, 3" by 10", reducing

above and below to a neck of 1" in diameter and holding approximately 1½ liters. They are submerged in the large square tank which rests on the base of the instrument and hence do not appear in the figure. A swinging pilot light is provided at left and right for simultaneous ignition of the burners. From 7 to 9 minutes are required for burning out the contents of the gas cylinders, the needle valves controlling the flames being finely adjusted so that the water-levels on the glass gauge may be made to stop exactly at any desired graduation. Corresponding graduations on the two gauges represent exact equivalents of gases. It is not necessary to know the exact volume in cubic centimeters, since it is only essential to have equivalent quantities. Since these quantities are subjected to the same temperature and pressure, the operation is independent of barometric conditions and room temperature. The only condition, therefore, not covered by the above provisions is the matter of varying radiation. For this element in the case, advantage is taken of the fact that the value for hydrogen, 325 B. t. u. per cu. ft., is very nearly half the value of ordinary house gas. Hence, by installing a double cylinder, or rather a third cylinder, of exactly equal volume with the other two gas containers and cross-connecting the same in such a way as to make it possible to burn two volumes on one side against one volume on the other, we are able to discharge under each heater almost exactly equivalent quantities of heat.

It will be evident also that for some types of gas, as a rich producer gas of approximately 300 to 350 B. t. u. per cu. ft. with hydrogen as the standard of comparison, equal volumes of each would be taken, while for lower-grade material of, say, 100 to 150 heat units, the reverse of the first condition would be called for and two volumes of the unknown gas would be burned against one volume of hydrogen. The advantage of using hydrogen is further seen in the availability of a pure product by generating the same from "Hydron," an alloy of sodium and lead which readily decomposes in a simple generator by contact with water yielding an exceptionally pure quality of standard gas.

As an illustration of the operation of this instrument, as well as affording a confirmation of the error brought out in the series on hydrogen in the Junker apparatus, a number of determinations are given in Table III, in which gas from the city supply was drawn simultaneously into each instrument and the B. t. u. determined in the prescribed manner for each apparatus, the new device using hydrogen as the standard on which calculations for that method were based. The tests extended over a number of days. The percentage of error is seen to be closely in accord with the relative temperatures of exhaust gases and the room. Where the exhaust tempera-

ture is lowest with reference to the room (2° lower as in No. 8), the percentage of error is also lowest, and where the exhaust gases are highest (2° above, as in No. 1), the percentage of error is highest. Thus, not only is the fact of the error confirmed, as shown in Table I, where the Junker is run on pure hydrogen, but also a marked consistency in the amount of error in each series is apparent, averaging approximately 3½ per cent. on the house gas and 4¼ per cent. with the hydrogen.

TABLE III.

Test No.	A Gas temp.	B. Room temp.	C. Exhaust temp.	D. J. per cu ft. Junker	E. B. t. u. per cu ft. Parr.	F. Diff. E - D	Per cent. of diff. E F × 100.
1	83	81	83	684	713	29	4.0
2	83	81	83	631	658	27	4.1
3	83	81	82	691	719	26	3.6
4	79	78	78	602	625	23	3.7
5	79	79	79	605	628	23	3.6
6	80	79	79	627	649	22	3.4
7	83	80	79	636	658	22	3.3
8	81	80	78	630	647	17	2.6

The results of Table III suggest another series of tests parallel with those of Table III, wherein the Junker apparatus was run under conditions indicated by the curve in Fig. 1; that is, to compensate for an average loss of 3½ per cent., or 22-24 B. t. u. for an average gas, a difference in temperature approximating 11 or 12 degrees would be called for as between the exhaust gas and the room. The results of this series are shown in Table IV:

TABLE IV.

Test No.	Gas temp.	Room temp.	Exhaust temp.	Degree lower for exhaust	B. t. u. per cu. ft. Junker.	B. t. u. per cu. ft. Parr.	Diff. in B. t. u.
1	80	79	67	-12	636	634	+2
2	80	80	67	-13	630	627	+3
3	80	80	67	-13	633	629	+4
4	80	79	67	-12	631	630	+1
5	81	79	67	-12	618	618	0
6	78	78	67	-11	627	627	0
7	78	78	66	-12	623	620	+3
8	78	78	66	-12	620	617	+3

From these results it would seem that for a gas averaging 650 B. t. u., the Junker apparatus would need to be operated in a manner to deliver the exhaust gases at from 10° to 12° lower than room temperature.

Concerning other features of the new apparatus, the indicated values are gross and not net. From the above showing of the tables it must be evident that any attempt to arrive at the net values by taking account of the water of condensation is an approximation only. Moreover, practically all authorities agree that the gross value is the basal factor and should be recognized as such. As for portability, it has been considered far more practicable to bring the gas to the instrument rather than attempt to carry the apparatus to the gas. Since only approximately 1½ liters are employed in each determination, this is seen to be entirely feasible. A new or



different sample of gas can be charged into the cylinder as free from contamination as is possible in the filling of a gas pipette. In regular operation upon city gas drawn directly from the service pipes, approximately 10 minutes is occupied in adjusting and reading the temperatures of the heaters and filling the gas cylinders. An additional length of time is used in burning out the gas volumes and reading the final temperatures.

I wish to acknowledge my indebtedness to Mr. N. W. Hill for the diligence and care exercised in deriving the data which accompanies this paper.

### DISSOLVING CHEMICALS AND AGITATING SOLUTIONS: SOME PROBLEMS IN THE MANUFACTURE AND AGITATION OF SULPHIDE SOLUTIONS.

By OSKAR NAGEL, Ph.D.

Received June 24, 1910.

Sulphide of barium is produced by reduction of barytes by means of powdered coal in a reverberatory furnace. In a suitable installation of this kind about 90 per cent. of the barytes may be reduced.

The crude mass obtained by reduction is never used as such, as the impurities—coal dust, etc.—contained therein are rather undesirable for all uses which sulphide of barium is put to. In the majority of cases the sulphide has to be brought into solution by means of water, and for many uses, such as the manufacture of barium salts, lithopone, etc., the solution should be as concentrated as possible. Hence the dissolving appliances most fit for this purpose should be of great interest to the respective industries, the more so as in most factories manufacturing these products rather primitive methods are used.

In order to elute the material perfectly, care has to be taken that the water is sprayed uniformly over the entire batch. Provision must be made for conveniently charging the material and discharging residue. The water used should be warm. Furthermore, the sulphide solution first obtained should circulate and pass several times through one or more batches of solid material, if possible, according to the countercurrent principle, in order to yield a somewhat concentrated solution.

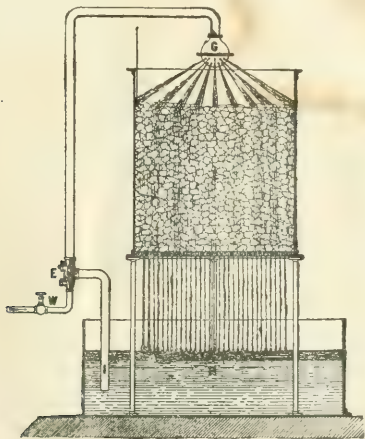


Fig. 1.

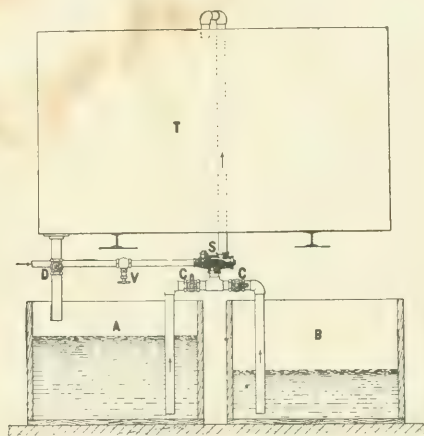


Fig. 2.



Fig. 3.

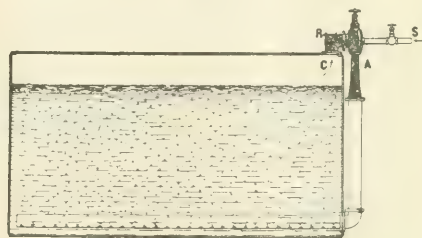


Fig. 4.

An installation in which all these points are considered is shown (in one unit) in Fig. 1; *L* is the vessel holding the material to be eluted. The material is charged at the top and discharged through a door or manhole. The water reaches the material through a spray, whereby a uniform elution is effected. The solid material is preferably supported by coarse filter cloth or perforated screens and the solution flows finally into tank *H*. The water is pumped to *L* by means of a steam-jet siphon, *E*, whereby the water or other liquid passing through the siphon is heated simultaneously. For starting up, tank *H* is partly filled with water and the steam valve opened. The steam issuing from a nozzle carries along the liquid to be transported, a considerable part of the momentum of the steam being utilized for conveying the liquid. After a short time tank *H* will contain a solution of sulphide, whereupon it may be again, by means of the same siphon, lifted and passed through *L*, which process, if only a single unit is at hand, may be repeated until the solution is obtained in the desired strength. Then the liquid can be removed from *H* and replaced by fresh water, which may be passed once through the solid (if the latter is not yet perfectly extracted); now *L* can be discharged, charged with fresh material and the process continued.

The manipulation will be considerably simplified if two tanks, *H*, or two vessels, *L*, are provided. It is readily understood that such an installation would be somewhat more elastic. An installation built along these lines is shown in Fig. 2. It shows the installation of a siphon, *L*, for lifting alternately from tanks *A* and *B*. *C* are the cocks, *T* the overhead tanks. The ideal way would be to have two, or preferably four, vessels, *L*, and two, or preferably four, tanks, *H*, as by such an installation if suitable "cross-wise" pipe connections are provided an absolutely elastic system is obtained which presents no difficulties to the use of the countercurrent principle.

The outside view of a siphon with flanged ends is shown in Fig. 3. The steam pressure to be used in connection with these siphons depends upon the height of lift and should equal in pounds the total elevation in feet. The minimum steam pressure is 20 pounds. This will pump to a height of 20 feet. The Schutte & Koerting Company, of Philadelphia, manufacture these siphons up to maximum suction of 24 feet. Water, when flowing to the siphon, may have a maximum temperature of 140° F.

The proportion of the steam to the water (or any other liquid of the same specific gravity) which is discharged varies according to the height of lift from (weight) 1.84 to 1.42. The increase of temperature of the liquid also changes accordingly from 15° to 32° F. The capacity of these siphons in gallons of water per hour is from 200 to 30,000.

For liquids of higher specific gravity the capacity is correspondingly lower.

In the manufacture of sulphides and other chemicals it is sometimes desirable to agitate liquids without causing any contact with air. Direct steam would always be satisfactory, but the immense steam consumption of the plain steam agitator prevents the use of this apparatus; the application of the ordinary steam jet blower, which furnishes a mixture of air and steam, is not permissible with substances that are oxidized by air. Hence the proper thing to use would be a steam-jet blower, which is connected to a supply of an indifferent gas. This, however, is too expensive, and the only solution of this problem that I know of is the one shown in Fig. 4. The tank *C* which contains the liquid to be agitated is provided with an air-tight cover, the space between liquid and cover being filled out by an indifferent gas. A so-called duplex steam-jet agitator is connected to the top of the tank. The steam passes through *S*, and the steam-jet issuing through nozzles provided in the body of the agitator draws in (at *C*) the indifferent gas; the mixture of gas and steam travels through *A* and passes through the perforations of the bottom pipe as shown in the figure, acting as an agitator of the liquid. The indifferent gas is always used over again, and is continuously circulated. This is evidently the most economical way to effect agitation without the admission of air.

### A ROTATING GRAPHITE ANODE.<sup>1</sup>

By J. W. TURRENTINE.

Received June 7, 1910.

Mention has already been made of designs of a rotating graphite anode which was to accompany the graphite cathode dish.<sup>2</sup> This piece of apparatus has now been made and is in use. Its serviceableness when employed in connection with the platinum Classen dish, as well as with the graphite cathode dish, is such that, although the anode is not yet perfected, this preliminary account of it is deemed warranted.

The graphite anode, it is hoped, may be found capable of supplanting the vastly more expensive platinum anode in electrochemical analysis and other electrochemical processes where the rotating anode is used. As has been pointed out, many of the beautiful and time-saving methods of electro-analysis and of electrochemical operation might fail of adoption because of the expense of the platinum apparatus involved. When graphite is employed the expense is minimized.

Little attention has been paid heretofore to special forms of anodes in electro-analysis. The efforts of

<sup>1</sup> A paper presented at the Seventeenth General Meeting of the American Electrochemical Society, at Pittsburgh, Pa., May 5-7, 1910.

<sup>2</sup> Turrentine, *J. Phys. Chem.*, **13**, 438 (1909). *Trans. Am. Electrochem. Soc.*, **15**, 505 (1909). *Chem. Abstr.*, **4**, 691 (1910).

the developers of this branch of electrochemistry have been directed rather towards perfecting the cathode. There are, therefore, several useful forms of cathodes which possess both of the desired qualities of lightness in weight and of large surface area. There is still, however, need of a cheap form of rotating anode which is constructed of some non-corrodible material and which presents a large surface area. The electrical resistance within the cell then may be so slight that currents of considerable strength may be passed without difficulty.

The chief advantage to be gained from rotating the anode instead of the cathode is that the anode is then placed above the cathode, instead of in the reverse order; the oxygen which is evolved from the former does not bubble over the surface of the latter and there oxidize the deposited metal. On the other hand, the stirring in the cathode region is not so effective when the anode is rotated as when the cathode is rotated. However, when the two poles are as close to each other as they are in the apparatus which is to be described in this paper, there can be but a very slight difference in the relative effectiveness of the stirring in the electrode regions.

By means of a rotating dish anode and a dish cathode, both of platinum and the two of the same general shape, Miss Langness<sup>1</sup> performed electro-analyses with current strengths as great as 16 amperes. A half gram of copper was precipitated with this apparatus in six minutes, and an equal amount of silver in two minutes. The results obtained showed a very good agreement with the theoretical values, and the time consumed was unprecedentedly short.

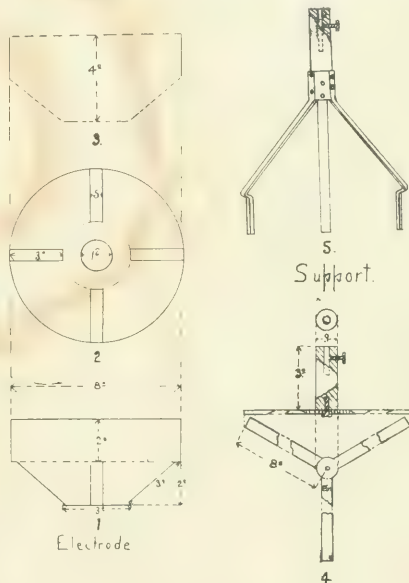
The anode used was fashioned from a platinum dish by cutting ten radial slits in its sides and by soldering, or otherwise fastening, across its top, a stout platinum wire, to the center of which was attached, T-wise, a perpendicular platinum rod to serve as the axis. This apparatus, being constructed of platinum, is expensive.

The anode which it is the purpose of this paper to describe is constructed of an especially hard grade of Acheson graphite. It is dish-shaped. It is cut from stick graphite, and is turned down on a lathe to the desired size and thickness.

The anode in use was designed to accompany the graphite cathode dish, and is constructed so as to conform in shape to the shape of that dish. Its diameter is 8 cm. and its depth 4 cm. For a depth of 2 cm. from the top the object is cylindrical (see Figs. 1, 2 and 3). The contour below the cylindrical portion is that of a truncated cone. The truncation serves as the base. The slope of the frustum reduces the diameter from 8 cm. at the bottom of the cylindrical portion to 3 cm. at the truncation. The lateral dimension of the cone is also 3 cm. In the walls of

the conical portion are cut four radial, equidistant slits. These extend from the lower edge of the cylindrical part to the edge of the base. In the base is also an opening, centrally placed, which is circular in shape and is 1.2 cm. in diameter.

The orifices permit the solution contained in the cell to flow into the interior of the electrode. However, when the anode is being rotated, the centrifugal force generated holds nearly all of the solution in the space outside the anode. When the cathode is also dish-shaped, this space may be quite narrow. Then, while the electrode rotates, practically the entire volume of the solution is held constantly within



the zone of activity between the two electrodes. The arrangement of the openings is also such that the effect of a Witt stirrer is produced. The solution is drawn into the interior of the anode through the lower, axially-placed opening in the bottom of the anode, where the centrifugal force is low, and is thrown out through the lateral slits, where the centrifugal force is high. Gravitational forces then bring the solution back to the bottom of the cell.

From these statements it may be inferred that the active surface of the electrode is the outside surface. This is practically true, though it has been noted, when the electrode has been used as a cathode for the deposition of metal, that some metal is deposited on the interior, in regions near the edges of the orifices.

The dish-like contour of the anode is of special advantage when the anode is used in connection with a cathode dish. The two poles may then be

<sup>1</sup> J. A. C. S., 29, 459 (1907).



brought quite close together along their entire surfaces. The distance through the solution traversed by the current is then very short, and the resistance is correspondingly low. The diameter of the anode is 8 cm. The diameter of the graphite cathode dish designed to be accompanied by the anode is 9.5 cm. The space between anode and cathode then may be as short as 0.75 cm.

The truncated conical shape of anode was planned with the thought in mind that perhaps an object with straight edges might be more easily cut than one whose periphery was a spherical section. Drawings of both the spherical and the truncated conical shape were given the manufacturers.<sup>1</sup> The one described has been chosen by them. A possible slight advantage of the hemispherical form is that a somewhat larger surface area is afforded per unit of weight of graphite, presupposing walls of equal thickness. The graphite anode which has been in use in this laboratory has walls of 1 mm. thickness, the same as those of the cathode dishes. Such a degree of thinness is undesirable on account of the lack of durability of the article. Nor is the thinness of the walls and the resulting lightness so important in the case of the anode as in that of the cathode, as the former rarely has to be weighed. The heavier the anode, however, the greater the weight will be on the bearings of the rotator and the more power will be required, consequently, to operate it. The best results could be obtained probably with walls of 2-3 mm. thickness. Such a thickness is recommended.

The surface area of the anode is, roughly, 80 sq. cm. Such a large electrode surface decreases the resistance in the cell.<sup>2</sup>

A very satisfactory form of support for the anode, made of aluminum, is now in use. To a solid aluminum cylinder, which serves as the axis, are fastened three aluminum prongs, equidistant apart. The axial cylinder is 4 cm. long and for 2.8 cm. of its length is 0.9 cm. in diameter; for the remaining distance it is 1.2 cm. in diameter. It is provided with a hole in its top, inserted axially, to accommodate the axis of an electric motor or other rotating device. A screw enters this opening at right angles, by means of which the connection with the motor may be made secure. To the lower, enlarged portion of the cylinder are fastened the three prongs by means of rivets. The prongs are 8 cm. long, 0.5 cm. wide, and 0.2 cm. in thickness. They extend downward and outward from the axis; the circumference of the circle described by their points when the support is rotated is somewhat larger than that of the anode. When these are pressed inward, the anode may be slipped over them. Then, on being released, they press outward against the inner walls

of the anode with sufficient force to hold it in position. Fig. 5 was drawn from this support.

A support of practically the same plan and of equal efficiency could be made by cutting the prongs in one piece from sheet aluminum and fastening this piece by means of a screw to the bottom of the cylindrical piece. The prongs could then be bent to the desired angle and shape. This method of manufacture is illustrated in Fig. 4.

The cylindrical piece is 3 cm. in length. The prongs should be cut as represented, each being about 8 cm. in length from their common center. Through this center passes the screw which fastens the prongs to the axis. The finished support would have very much the same appearance as that shown in Fig. 5.

The aluminum support so far has been found entirely satisfactory. It is not necessary that the ends of the prongs should come into contact with the solution at all, this depending on the depth of the solution inside the anode. Yet, when they do, the corrosion is extremely slight, as aluminum becomes passive in solutions of most electrolytes. Nor would the presence of small amounts of aluminum in the solution undergoing electrolysis prove disadvantageous. The oxidation of the aluminum does not become sufficient to interfere with the electrical contact between the aluminum and the graphite. Should the solubility of the aluminum make its use prove undesirable, other metals could be substituted in part or in whole. The tips of the prongs could be covered with platinum foil without very materially increasing the expensiveness of the apparatus.

As suggested, the rotation is effected by fastening the support directly to the shaft of a small electrical motor of the "Ajax" type. This is the simplest and is perhaps the cheapest arrangement. Current may be admitted to the motor from a 110-volt circuit through incandescent lamps as resistance. By means of lamps of low candle power, the current, and, therefore, the speed of the motor, may be regulated satisfactorily. Electrical connection is made with the anode through the metal bearings of the motor, or by means of a brush playing on the aluminum support. The insulation in such cheap motors is often so poor that leakage currents from the circuit operating the motor may find their way through the solution undergoing electrolysis. This tendency may be controlled or entirely overcome by a suitable arrangement of the electrical connections and the resistance controlling the electrolyzing current.

The rotating apparatus here described affords a perfectly smooth agitation of the solution and causes no spattering; only that arising from the liberation of a large volume of gas is noticed.

The qualities possessed by graphite which make it a desirable substance of which to construct an anode are its absolute insolubility, its cheapness and its high

<sup>1</sup> Messrs. Eimer & Amend, New York.

<sup>2</sup> Turrentine, "The Meaning of Current Density," *J. Phys. Chem.*, **14**, 152 (1910).

conductivity. Platinum is usually accepted as the more nearly ideal metal for use as a non-attackable anode. However, it can no longer be regarded as an insoluble metal, although for most electrolyses, where its behavior is known beforehand, it is entirely satisfactory. Anodes of other metals plated with platinum would be both expensive and quite untrustworthy.

The objections to graphite so far discovered are its porosity and its tendency to flake off at high current densities.

While porosity would be quite non-permissible in a cathode, it need not be such an objection in an anode. This is especially true where the anode is being used exclusively in solutions of the same character. Under these conditions no impurities would be introduced by absorbed materials entering the solution from the anode. However, the porosity of the graphite has been practically entirely overcome by the treatment with paraffin or ceresine already described.<sup>1</sup>

The disintegration of the graphite at the anode is noticed only at high current densities. This would be objectionable because it would mean the eventual destruction of the anode. Likewise it is conceivable that in quantitative electro-analyses of metals, particles of graphite would be occluded by the depositing metal and the weight of the latter thereby increased. Yet this phenomenon is noticed only at high current densities, and the large surface area of the graphite anode makes possible the use of large current strengths without at the same time producing high current densities.

The problem, how to prevent the "flaking off" of the graphite, is now being investigated in this laboratory. Electrodes treated in various ways to render them more resistant are being compared with each other under like conditions in solutions of various electrolytes and at various current densities. The results so far obtained would indicate that no disintegration occurs with a paraffined graphite anode under a current density of 6 amperes per square decimeter. With the anode described, then, a current of at least 5 amperes may be employed with impunity.

It has been thought by some that paraffining graphite would decrease its conductivity. While probably no accurate measurements have been made to determine the effects of paraffining on the conductivity, that property of the graphite is not conspicuously impaired. It appears that the resistance of the solution and that due to polarization phenomena are so great in comparison with that produced by the presence of the paraffin that the latter resistance is entirely negligible.

The anode as described has been employed with success in numerous electrochemical processes, in electrochemical analyses and separations of metals

and in electrochemical oxidations. It has been employed also as a rotating cathode. In its present state of development it has shown itself a useful piece of apparatus. After further experimentation it is hoped that its present defects may be overcome so that it may be given an unqualified recommendation.

WESLEYAN UNIVERSITY  
April, 1910.

#### A COMPARISON OF THE EFFICIENCY OF OTTO PFEIFFER'S AND DENNIS & MCCARTHY'S METHOD FOR DETERMINING BENZENE IN ILLUMINATING GAS.

By E. P. HARDING AND CARL TAYLOR.  
Received June 21, 1910.

In determining the benzene vapors in Minneapolis illuminating gas (which is a mixture of carburetted water gas and coal gas) by the Dennis and McCarthy method, it was found that by passing the gas back and forth in the nickel ammonium cyanide pipette and subsequently in the 5 per cent. sulphuric acid pipette that if this process was continued longer than two minutes in either pipette, a higher result was obtained than if the process was continued for exactly two minutes, which was contrary to the results obtained by Dennis and McCarthy.<sup>1</sup> These observations led the writers of this paper to determine the benzene in the gas by a more exact method and to compare the results with those obtained by the above-mentioned method, and to an investigation of the cause of the increased and varying results obtained by a longer absorption than two minutes.

The principle of the Dennis and McCarthy method is the absorption of the benzene in a nickel ammonium cyanide solution passing the gas back and forth in the pipette for about two minutes and then passing it back and forth into a pipette containing a 5 per cent. solution of sulphuric acid for about two minutes.

The exact method used was that of Otto Pfeiffer,<sup>2</sup> the principle of which is the oxidation of the benzene to dinitrobenzene, the separation of the dinitrobenzene with ether and its reduction to diamidobenzene in an alcohol solution with a standard hydrochloric acid solution of stannous chloride and the determination of the excess of stannous chloride by titrating with a N/10 normal solution of iodine.

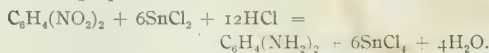
The method in detail is as follows: An accurately calibrated separatory funnel of about 500 cc. capacity is filled with gas. The funnel is inverted and 2 cc. of mixed sulphuric and nitric acids (equal volumes of concentrated  $H_2SO_4$  and fuming  $HNO_3$ ) are introduced into the outlet tube and carefully run into the separatory funnel. The funnel is rotated so as to distribute the acids as much as possible over the

<sup>1</sup> J. A. C. S., **30**, 233.

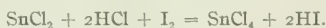
<sup>2</sup> Chem. Zeit., **76**, 884.

<sup>1</sup> "A Graphite Cathode Dish," *Loc. cit.*

inner surface and then allowed to stand one-half hour. It is then inverted and 30 cc. of concentrated soda solution carefully introduced and the funnel shaken until the vapor formed disappears. If the solution is still acid it is neutralized with the soda solution and then rendered just acid with hydrochloric acid. The dinitrobenzene is then separated by extracting successively with small amounts of pure ether and the ethereal extracts run into a small flask to which is added one gram of dry potash and about one-half gram of animal (blood) charcoal. After repeated shaking the solution is filtered into a 200 cc. flask, the filter washed with ether, and the ether completely removed in a water bath. About 10 cc. of alcohol and exactly 10 cc. of stannous chloride solution (150 grams of tin dissolved in hydrochloric acid plus 50 cc. of hydrochloric acid, and made up to one liter with water) are added and the flask heated in a water bath for ten minutes. The solution is then made up to the 200 cc. mark and 20 cc. titrated with N/10 iodine solution, using starch as an indicator. The reaction between the stannous chloride and the dinitrobenzene takes place according to the following equation:



A blank experiment is made by heating 10 cc. of the stannous chloride solution with alcohol, diluting to 200 cc. and titrating 20 cc. with the standard iodine solution. The reaction between the stannous chloride and the iodine takes place according to the reaction



In determining the benzene the writers of this paper used an absorption funnel of 1202.7 cc. capacity and the proportionate amounts of sulphuric and nitric acids. Ten cc. of stannous chloride solution were added to the dinitrobenzene solution which was then diluted to 500 cc. instead of 200 cc. and 10 cc. taken for titration. This dilution made much less difference between the strength of the stannous chloride and iodine solutions resulting in a greater accuracy in titrating.

In comparing the results obtained by the two methods the gas was passed back and forth in the fuming sulphuric acid pipette containing the nickel ammonium cyanide for exactly two minutes and then in the sulphuric acid pipette for exactly two minutes. The results obtained were as follows:

	Otto-Pfeiffer method. Per cent of benzene.	Dennis and McCarthy method. Per cent of benzene.
Nov. 29, 1909.....	1.59	1.4
Dec. 1, 1909.....	1.87	1.8
Dec. 4, 1909.....	1.0	1.5
Dec. 15, 1909.....	0.67	0.80
Dec. 15, 1909.....	0.75	0.80
Dec. 17, 1909.....	1.20	1.25

The carbon dioxide, benzene, and unsaturated hydrocarbons were absorbed by the respective absorbents—potassium hydroxide, nickel ammonium cyanide, and bromine water—with the subsequent removal of the bromine vapors with potassium hydroxide and these results compared with those obtained by passing the gas successively into the nickel ammonium cyanide pipette for different lengths of time and then into the sulphuric acid pipette for two minutes, with the following observations:

Dec. 6. I.	(1) Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	2.7	2.6
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.1	1.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 4 min. $\text{H}_2\text{SO}_4$ 4 min.....	1.3	1.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 11 min. $\text{H}_2\text{SO}_4$ 5 min.....	1.9	1.9
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 16 min. $\text{H}_2\text{SO}_4$ 6 min.....	2.2	2.2
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 31 min. $\text{H}_2\text{SO}_4$ 8 min.....	2.8	2.8
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 46 min. $\text{H}_2\text{SO}_4$ 10 min.....	3.3	3.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 66 min. $\text{H}_2\text{SO}_4$ 12 min.....	4.0	4.0
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	9.9	7.0

Dec. 8. II.	(1) Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	2.8	2.8
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.1	1.2
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 9 min. $\text{H}_2\text{SO}_4$ 4 min.....	2.0	2.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 19 min. $\text{H}_2\text{SO}_4$ 6 min.....	3.0	3.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 29 min. $\text{H}_2\text{SO}_4$ 8 min.....	3.5	3.5
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 39 min. $\text{H}_2\text{SO}_4$ 10 min.....	3.8	3.8
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 59 min. $\text{H}_2\text{SO}_4$ 12 min.....	4.2	4.2
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	9.6	6.7

Dec. 14. III.	(1)* Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	2.6	2.5
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.3	1.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 12 min. $\text{H}_2\text{SO}_4$ 4 min.....	2.0	2.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 22 min. $\text{H}_2\text{SO}_4$ 6 min.....	3.2	3.2
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 32 min. $\text{H}_2\text{SO}_4$ 8 min.....	3.7	3.7
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 57 min. $\text{H}_2\text{SO}_4$ 10 min.....	4.3	4.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 87 min. $\text{H}_2\text{SO}_4$ 12 min.....	4.9	4.9
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	9.9	6.3

March 31. IV.	(1) Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	2.4	2.5
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.4	1.5
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 7 min. $\text{H}_2\text{SO}_4$ 7 min.....	2.0	2.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 17 min. $\text{H}_2\text{SO}_4$ 6 min.....	2.6	2.6
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 27 min. $\text{H}_2\text{SO}_4$ 8 min.....	3.1	3.1
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 37 min. $\text{H}_2\text{SO}_4$ 10 min.....	3.7	3.7
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	10.6	8.3

Dec. 23. V.	(1) Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	2.2	2.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.3	1.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 13 min. $\text{H}_2\text{SO}_4$ 4 min.....	2.3	2.3
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 33 min. $\text{H}_2\text{SO}_4$ 6 min.....	3.5	3.5
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 30 hrs. $\text{H}_2\text{SO}_4$ 8 min.....	6.7	6.7
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 31 hrs. $\text{H}_2\text{SO}_4$ 10 min.....	6.7	6.7
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	9.2	...

April 5. VI.	(1) Per cent.	(2) Per cent.
$\text{CO}_2$ by KOH 2 min.....	3.0	3.0
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 2 min. $\text{H}_2\text{SO}_4$ 2 min.....	1.2	1.2
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 10 min. $\text{H}_2\text{SO}_4$ 4 min.....	2.8	2.8
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 20 min. $\text{H}_2\text{SO}_4$ 4 min.....	3.6	3.6
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 30 min. $\text{H}_2\text{SO}_4$ 6 min.....	4.4	4.4
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 40 min. $\text{H}_2\text{SO}_4$ 8 min.....	5.1	5.1
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 50 min. $\text{H}_2\text{SO}_4$ 10 min.....	5.7	5.7
$\text{C}_2\text{H}_6$ by $\text{Ni}(\text{CN})_2\text{NH}_3$ 60 min. $\text{H}_2\text{SO}_4$ 12 min.....	5.7	5.7
Unsat. hydrocarbons by Br water 7 min.		
KOH 1 min.	9.9	5.6



The illuminating gas was passed into the nickel ammonium cyanide pipette for two minutes, then repeatedly into the sulphuric acid pipette for varying periods of time with the following results:

Nov. 5. VII		Per cent	
CO <sub>2</sub> by KOH 2 min	.....	2	0
C <sub>6</sub> H <sub>6</sub> by Ni(CN) <sub>2</sub> NH <sub>3</sub> 2 min. H <sub>2</sub> SO <sub>4</sub> 2 min.	.....	1	0
H <sub>2</sub> SO <sub>4</sub> 5 min.	.....	1.4	
H <sub>2</sub> SO <sub>4</sub> 10 min.	.....	1.6	
H <sub>2</sub> SO <sub>4</sub> 16 min.	.....	2.0	
H <sub>2</sub> SO <sub>4</sub> 22 min.	.....	2.4	
H <sub>2</sub> SO <sub>4</sub> 27 min.	.....	2.8	
H <sub>2</sub> SO <sub>4</sub> 31 min.	.....	3.3	
H <sub>2</sub> SO <sub>4</sub> 36 min.	.....	3.8	
H <sub>2</sub> SO <sub>4</sub> 48 min.	.....	4.6	
		(1)	(2)
		Per cent.	Per cent.
April 5. VIII.			
CO <sub>2</sub> by KOH 2 min.	.....	3.0	3.1 3.0
C <sub>6</sub> H <sub>6</sub> by Ni(CN) <sub>2</sub> NH <sub>3</sub> 2 min. H <sub>2</sub> SO <sub>4</sub> 2 min.	.....	1.2	1.3 1.3
H <sub>2</sub> SO <sub>4</sub> 4 min.	.....	1.5	1.4
H <sub>2</sub> SO <sub>4</sub> 6 min.	.....	1.6	1.6
H <sub>2</sub> SO <sub>4</sub> 8 min.	.....	1.7	1.7
H <sub>2</sub> SO <sub>4</sub> 10 min.	.....	1.7	1.8
H <sub>2</sub> SO <sub>4</sub> 12 min.	.....	1.9	1.9
H <sub>2</sub> SO <sub>4</sub> 14 min.	.....	2.0	2.0
Unsat. hydrocarbons by Br water 7 min.	.....		
KOH 1 min.	.....	9.9	9.2 9.1
		(1)	(2)
		Per cent.	Per cent.
April 5. IX.			
CO <sub>2</sub> by KOH 2 min.	.....	3.1	..
C <sub>6</sub> H <sub>6</sub> by Ni(CN) <sub>2</sub> NH <sub>3</sub> 2 min. H <sub>2</sub> SO <sub>4</sub> 2 min.	.....	1.2	1.2
H <sub>2</sub> SO <sub>4</sub> 4 min.	.....	1.4	
H <sub>2</sub> SO <sub>4</sub> 6 min.	.....	1.6	
H <sub>2</sub> SO <sub>4</sub> 8 min.	.....	1.7	
H <sub>2</sub> SO <sub>4</sub> 10 min.	.....	1.9	
H <sub>2</sub> SO <sub>4</sub> 12 min.	.....	2.1	
H <sub>2</sub> SO <sub>4</sub> 14 min.	.....	2.3	
Unsat. hydrocarbons by Br water 7 min.	.....		
KOH 1 min.	.....	9.9	

In comparing the percentages of unsaturated hydrocarbons in 1 and 2 of each determination in the foregoing tables it will be observed that each respective difference is equal to the increased absorption after the first two minutes of absorption, respectively, in the nickel-ammonium-cyanide and sulphuric acid pipettes. These differences are shown by the following tabulation:

I.	II.	III.
9.9—7.0 = 2.9 cc.	9.6—6.7 = 2.9 cc	9.9—6.3 = 3.6 cc.
4.0—1.0 = 3.0 cc	4.2—1.2 = 3.0 cc	4.9—1.3 = 3.6 cc
10.6—8.3 = 2.3 cc.	9.9—5.6 = 4.3 cc.	{ 9.9—9.2 = 0.7 cc
3.7—1.5 = 2.2 cc	5.7—1.2 = 4.5 cc.	{ 2.0—1.3 = 0.7 cc
		{ 9.9—9.1 = 0.8 cc
		{ 2.0—1.3 = 0.7 cc

From these observations it is evident that the nickel-ammonium-cyanide and sulphuric acid each continue the absorption after the first two minutes and that this increased absorption is due to the unsaturated hydrocarbons present.

Unsaturated hydrocarbons were prepared and, unmixed with air or illuminating gas, their rate of absorption determined respectively in nickel-ammonium-cyanide and sulphuric acid.

Ethylene was prepared by heating a mixture of alcohol and concentrated sulphuric acid and purified

by passing it successively through sulphuric acid and potassium hydroxide. To insure a complete purification, the gas was shaken successively in pipettes containing potassium hydroxide and sulphuric acid immediately before determining its rate of absorption. The following results were obtained:

	(1)	(2)
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	1 min. 0.3 cc.	2 min. 0.8 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	2 min. 0.9 cc.	4 min. 1.3 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	3 min. 1.3 cc.	6 min. 2.0 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	4 min. 2.0 cc.	8 min. 2.7 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	5 min. 2.4 cc.	10 min. 3.4 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	7 min. 2.8 cc.	12 min. 4.0 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	9 min. 3.3 cc.	14 min. 4.7 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....		16 min. 5.4 cc.
Ethylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....		18 min. 6.2 cc.

	(1)	(2)
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	2 min. 3.3 cc.	2.5 cc.
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	4 min. 6.0 cc.	4.9 cc.
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	6 min. 8.3 cc.	8.1 cc.
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	8 min. 10.7 cc.	10.9 cc.
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	10 min. 13.2 cc.	12.3 cc.
Ethylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	12 min. 15.5 cc.	

Pure acetylene was prepared and its rate of absorption determined with the following results:

Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	1 min. 4.3 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	2 min. 8.5 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	6 min. 25.1 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	11 min. 45.2 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	16 min. 63.7 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	26 min. 87.2 cc.
Acetylene with Ni(CN) <sub>2</sub> NH <sub>3</sub> .....	31 min. 94.6 cc.

	(1)	(2)
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	1 min. 22 cc.	....
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	2 min. 41 cc.	40 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	3 min. 65 cc.	68 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	4 min. 72 cc.	75 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	5 min.	83 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	6 min.	91 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	7 min.	95 cc.
Acetylene with 5 per cent. H <sub>2</sub> SO <sub>4</sub> .....	8 min. 96 cc.	

These hydrocarbons are each soluble in a pure state in nickel-ammonium-cyanide and 5 per cent. sulphuric acid.

It is concluded that the Dennis and McCarthy method for determining benzene in coal gas is accurate if the gas is left respectively in the nickel-ammonium-cyanide and sulphuric acid pipettes for exactly two minutes; that if left a longer time than two minutes an increased absorption takes place and that this increased absorption is due to the unsaturated hydrocarbons which is contrary to the observations of Dennis and McCarthy.<sup>1</sup>

In all these determinations a 100 cc. sample was used and measured in a Hempel pipette. The solutions were saturated with the gas before using, and no corrections were made for the slight changes in volume caused by slight changes in temperature and pressure.

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<sup>1</sup> J. A. C. S., 30, 233.

# THE RAPID DETERMINATION OF LEAD IN ORES BY ELECTROLYSIS WITH STATIONARY ELECTRODES.

By R. C. BENNER.

Received May 9, 1910.

The determination of lead by electrolysis, when weighed as the peroxide, has, in the past, been uncertain. Nearly all investigators have found the use of a different factor necessary, but in no case has the use of the theoretical been allowable.

When the peroxide is deposited on a dish it is possible to ignite and weigh as the monoxide with excellent results,<sup>1</sup> but with the gauze electrode it is impossible to make the ignition over the Bunsen flame in a satisfactory manner. Sand<sup>2</sup> has been able to deposit the peroxide in such a condition that the error caused by the use of the theoretical factor when working with small amounts of lead is negligible. This was accomplished by depositing from a solution free from ammonium nitrate and the oxides of nitrogen, at a temperature of from 94° to 97° C., using a current of five amperes. When the deposition was performed under these conditions he used the factor 0.8651 after drying the deposit with alcohol and ether.

Recently, in the western part of the United States, the electrolytic method has been used to a great extent for the determination of lead in ores; therefore, a rapid means of carrying out this determination is of interest.

A lead nitrate solution containing 0.2508 gram of lead in 10 cc. was prepared, in order that the gauze electrode<sup>3</sup> might be experimented with. The following determinations were made in 75 cc. of solution, in the presence of 103 cc. of nitric acid (sp. gr. 1.40) with a current of 4.8 amperes and 2.5 volts. The electrolyte was warmed during the deposition, so that the temperature of the cell was kept just below the boiling point, *e. g.*, the highest temperature at which it is possible to carry on the electrolysis without the liberation of the oxides of nitrogen, which, according to Sand,<sup>3</sup> tends to make the deposit non-adherent. The results below verify those obtained by Sand and give an idea of the accuracy of the method:

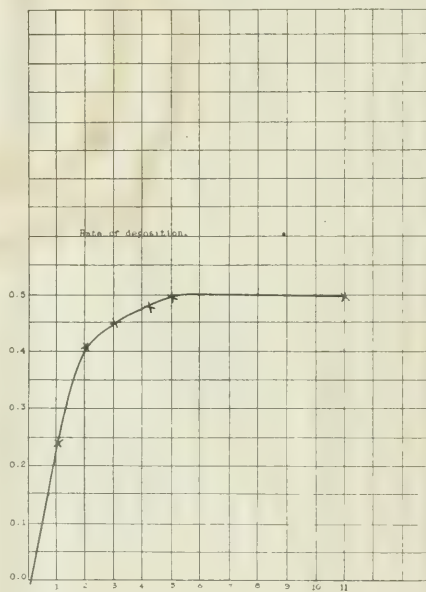
PbO <sub>2</sub> found.	Equivalent to Pb. Factor 0.886.	Pb taken	Time
0.2889	0.2502	0.2508	13
0.2905	0.2516	0.2508	20
0.2903	0.2513	0.2508	20
0.5814	0.5035	0.5017	20
0.5797	0.5020	0.5017	25
0.8734	0.7864	0.7525	25
0.8715	0.7547	0.7525	25

The rate of precipitation was determined with a current of 3.5 volts and 4.2 amperes at a temperature between 94 and 97° C. The solution in each

case contained 0.5018 gram of lead and 10 cc. of concentrated nitric acid and had a volume of 75 cc.:

Time. Min.	Lead taken.	RATE OF PRECIPITATION.	
		Lead deposited. Factor 0.886:	Peroxide deposited.
1	0.5008	0.2412	0.2789
2	0.5008	0.4126	0.4766
3	0.5008	0.4536	0.5237
4 1/2	0.5008	0.4871	0.5623
5	0.5008	0.5012	0.5787
11	0.5008	0.5007	0.5782

These results show that it is possible to deposit all of the lead, which can occur in a 0.5000 gram sample of ore, in from 5 to 10 minutes. In this case, as with copper, by far the greater part of the lead was deposited in the first few minutes. 90 per cent. was deposited in the first 3 minutes, while the remaining 10 per cent. took 3 minutes longer.



It was possible to remove all of the sulphur from galena as well as from some other sulphides, in form of hydrogen sulphide, by warming with hydrochloric acid (2 to 1). This made it possible to use the following process for those ores which contain no interfering sulphides. From 0.5 to 1.0 gram of the finely pulverized ore was weighed out, warmed with 15 to 20 cc. of hydrochloric acid (2 to 1) until completely disintegrated and all of the sulphur evolved as hydrogen sulphide, but not concentrated so far that the lead chloride crystallized out (this caused violent bumping). Then 20 cc. of concentrated nitric acid were added and boiling continued until all of the hydrochloric acid was expelled and the nitric

<sup>1</sup> Treadwell, "Analytical Chemistry," New York, 1904, Vol. II, p. 140

<sup>2</sup> Chem. News, 100, 269.

<sup>3</sup> THIS JOURNAL, 2, 195.

acid had a volume of 10 cc. It was then diluted to 75 cc. and electrolyzed in the usual manner. Those ores containing sulphides, which rendered the use of the preceding method impossible, were disintegrated with nitric and hydrochloric acids, 15 cc. of sulphuric acid added and the solution evaporated until heavy white fumes of sulphuric anhydride were evolved. After cooling, 50 cc. of water were added; it was boiled until all of the basic iron sulphate was dissolved, then the solution was diluted to 200 cc., filtered, and washed free from sulphuric acid. (As much lead sulphate as possible was left in the beaker and washed by decantation.) The lead sulphate was washed from the filter with the smallest possible amount of water into the beaker containing the bulk of the sulphate. Then 10 cc. of a warm saturated solution of ammonium carbonate were poured through the filter, received in the beaker containing the lead sulphate and warmed until all of the sulphate was converted to the carbonate. The lead carbonate was then filtered through the same paper, washed with water until nearly free from ammonium carbonate, dissolved in 40 cc. of nitric acid (1 to 3), the filter paper washed free from lead and the solution electrolyzed in the usual way. The following results on a lead ore containing copper show the accuracy of the method:

Analysis of the ore by ordinary methods: Ore No. 1—2.70 per cent. copper, 21.50 per cent. lead. Ore No. 2—2.28 per cent. copper, 22.20 per cent. lead.

Electrolytic determination of lead: Ore No. 1—21.52, 21.51, 21.59. Ore No. 2—22.20, 22.06.

Where it was desired to do away with the use of the factor and, at the same time, use the electrolytic method of determination, it was possible to do so by igniting, in a muffle, or small electric oven at a temp. of about 500° C., the gauze electrode on which the peroxide had been deposited. The following results show the accuracy of this modification of the electrolytic method:

Lead taken.	Lead found.
0.2509	0.2511
0.2509	0.2506
0.5018	0.5035
0.5018	0.5026
0.7527	0.7518

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# THE VALUE OF A CHEMICAL ANALYSIS AS SHOWN IN TRACING THE CAUSE OF A TYPHOID FEVER EPIDEMIC IN GEORGIA.

By H. B. ARBUCKLE.  
Received June 25, 1910.

Last October a sudden and virulent outbreak of typhoid fever occurred in a college community in Georgia, four institutions being simultaneously affected.

It was thought at first that some form of food supplies, as canned goods, which were served uncooked, was responsible for the epidemic, but chemical and bacterial examinations of all the canned supplies placed them above suspicion. A competent bacteriologist went over the situation and after carefully examining the dairy products, the pantry, the sanitary arrangements and the water supply, issued a written statement to the effect that as far as his investigation went no local cause was discovered. Already twenty had contracted fever, and three to four cases were being reported daily.

At this point the author undertook an investigation in which he was ably assisted by the local physician, Dr. Mary Sweet, who furnished a comprehensive history of each case. The data showed that all the cases were located in two brick dormitories which housed about 75 per cent. of the students. These buildings were infested with ants, while the others were not, and it was thought probable that these pests were distributing the bacilli, but experiments with a large number of ants, collected in many parts of both buildings, gave no indication of pathogenic germs.

Another examination of the pantry, the dairy and its products, confirmed the first and showed very satisfactory conditions. By this time the situation had become so serious that it was deemed wise to boil the water, milk and butter, as well as to sterilize every particle of food by thorough cooking.

The water supply, obtained from a well, was next taken up, although the bacterial examination was considered satisfactory by the local physician. The first chemical test applied to the drinking-water placed it under suspicion, as it showed high nitrites, a rough quantitative test giving one-tenth of one part per million, which is quite unusual in waters of the vicinity. Chlorides were present in unusual quantity and free ammonia was far above the amount found in a normal water of the vicinity. All of these data indicated pollution of the well water and gave a starting point for further investigation.

The well from which the drinking-water is obtained is forty feet deep, situated over fifty feet from the buildings, and on the opposite of the water-shed from the sewers. This well was cleaned twice during each year and was carefully cased with brick and cement for three feet above ground. The well and pump appeared to be in good condition.

The investigation was pushed in every direction. One hundred and fifty feet from the well supplying the drinking-water was an old well, kept as a protection against fire. The water of this well was examined and the quantities of nitrites, free ammonia and chlorides were even greater than those found in the first well, giving conclusive evidence of recent sewage pollution. Samples of water from both



wells were sent to the Johns Hopkins Bacteriological Laboratory. Their report confirmed that of the local bacteriologist in regard to the drinking-water: "There were found no distinct traces of pathogenic germs," but concerning the water from the old well the statement is: "We find strong presumptive evidence of the presence of *Bacilli Coli* and would condemn the water as badly contaminated." In the meantime, the author had had the sewers leading from the dormitory nearest the old well uncovered, and in one sewer, at a point within eight feet of the wall of the well, was found a broken joint and a hole in the side of the sewer an inch in diameter. A connection between the two wells was proved by introducing three pounds of potassium iodide into the old well and after one hour detecting iodine in the water of the well from which the drinking supply was obtained.

Two weeks after the sewer was repaired the chlorides in the well used for drinking-water had fallen from 57 parts to 15 parts per million. Another fact which strengthens the conclusion that the fever was caused by the drinking-water is that the last case was reported on the twentieth day from the date when boiling the water was begun. No straggling cases appeared. It was also found that a student, who had come to the college two weeks previous to the outbreak and just after recovery from a severe attack of typhoid fever, roomed in the building served by the broken sewer.

One beneficial result of this investigation was the abandoning of many shallow wells as a source of domestic supply.

A table of partial analyses of water from a number of wells in the town is given below, all of which, with the exception of two, the Childers and the Lovejoy wells, show serious pollution.

This article has been written not only to show the use chemistry may be to the epidemiologist but to bring again to the attention of sanitarians that while bacteriology gives much information regarding continuous pollution of a water supply, it is useless in giving knowledge of past pollution or past history of a water.

[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

## RELATION OF POT EXPERIMENTS TO THE ACTIVE PHOSPHORIC ACID OF THE SOIL.<sup>1</sup>

By G. S. FRAPS.

Received June 9, 1910.

By active phosphoric acid we here mean the phosphoric acid extracted by digestion of 200 grams of soil for five hours at 40° C. with 2000 cc. N/5 nitric acid without correction for neutralization. Factors which affect this method have previously been discussed.<sup>1</sup>

For about four years we have been conducting pot experiments upon a variety of Texas soils, and it is our purpose here to compare the results of these pot experiments with our chemical work.

### METHOD OF WORK.

Five kilograms soil were placed in a Wagner pot which had previously received 2 kilograms gravel. To one pot was added 2½ grams acid phosphate, 1 gram nitrate of soda, and 1 gram sulphate of potash. To another pot was added nitrate of soda and sulphate of potash. A comparison of the growth of the crop in these two pots shows the effect of phosphoric acid. Other pots were included in this work, but the description of them is foreign to the purpose of this article. Each pot received the same weight of seed and equal amounts of water. The water content was maintained during the growth of the crop by adding a sufficient quantity three times a week to restore the loss of weight. The pots were kept in glass or canvas houses. At the end of the period the crops were harvested, dried, weighed, and, in many cases, subjected to analysis.

### DEFICIENCY OF SOILS.

The weight of the crop without phosphoric acid divided by the weight with phosphoric acid gives the extent of deficiency. If the unfertilized crop is 50 per cent. or less of the fertilized crop, the soil is regarded as very deficient (DD); if less than 90 per cent., as deficient (D); and if more than 90 per cent., not deficient (S).

Several crops were sometimes grown on the same soil. In finally deciding on the deficiencies for soils, all crops grown upon the soil were considered and also any other circumstances which may affect the conclusions.

We have divided the soils into groups, according to their content of active phosphoric acid. Group 1 contains soils having less than 10 parts active phosphoric acid per million; group 2, less than 20; group 3, less than 30; and so on.

The results of our pot tests are combined in Table I, in which the number of soils decided to be very

<sup>1</sup> Full details of this work will be published in Bull. 126 of the Texas Experiment Station.

<sup>1</sup> *Am. Chem. J.*, 32, 1; *J. A. C. S.*, 28, 823.

Parts per million.

Waters analyzed.	Chlorine in chlorides.	Nitrogen in nitrites.	Ammonia (free).	Ammonia (albuminoid).
Storage well at college, break in sewer 8 ft. distant.....	167.5	0.24	0.544	0.095
Well used for drinking water at college .....	57.4	0.15	0.236	0.09
Blanchard well.....	106.0	0.02	0.12	0.07
Donnell well.....	110 <sup>1</sup>	0.015	0.10	0.09
Gaines well.....	35.6	0.02	0.095	0.08
Hathaway well.....	64.0	trace	0.09	0.06
Childers well.....	18.5	none	0.06	0.06
Lovejoy well.....	10.0	none	0.07	0.05
Town water (creek is source of supply).....	3.15	none	0.008	0.08

<sup>1</sup> A servant had thrown salt in this well.

deficient, deficient and not deficient, are given. Also the percentages of the total number in the group is given.

Of the 38 soils containing less than 20 parts per million of active phosphoric acid, we find 32 highly deficient, five deficient, and 1 sufficient. The sufficient soil had only one pot experiment made on it, with mustard, and the results might very possibly have been deficient had more tests been made.

*Soils containing 20 parts per million, or less, of active phosphoric acid are highly deficient in phosphoric acid.*

Considering the table further, we find that the percentage of very deficient soils decreases rapidly from 87 per cent. in the first group to 14 per cent. in the fourth, after which it decreases slowly to the 11-17 group, after which there is a sudden increase. One soil, however, makes a great difference in the percentage in these groups.

TABLE I.—NUMBER AND PERCENTAGE OF DEFICIENT SOILS GROUPED ACCORDING TO CONTENT OF ACTIVE PHOSPHORIC ACID.

Group.	Number of soils.			Percentage of soils in Group.		
	DD.	D.	S.	DD.	D.	S.
No. 1.....	13	2	0	87	13	0
No. 2.....	19	3	1	83	12	4
No. 3.....	7	10	1	39	55	6
No. 4.....	1	5	1	14	71	15
Nos. 5-6.....	1	4	2	14	57	28
Nos. 7-8.....	2	13	0	13	87	0
Nos. 9-10.....	1	5	2	13	63	24
Nos. 11-19.....	1	5	5	9	45	46
Nos. 32-42.....	2	0	4	33	0	66
Total.....	48	47	16			

The percentage of non-deficient soils increases with fair regularity throughout the table, though there are some breaks, notably in group 7-8.

In groups 3 to 10 are fifty-five soils, twelve of which are very deficient, 37 are deficient, and 6 appear to yield sufficient phosphoric acid; that is to say, about eleven per cent. are not deficient. The average corn crop without phosphoric acid is from 34 to 71 per cent. of that with phosphoric acid. We feel justified in drawing the following conclusions:

Soils containing from 30 to 100 parts per million of phosphoric acid soluble in N/5 nitric acid, are, as a rule, deficient in phosphoric acid, and the extent of their deficiency is related to the quantity of active phosphoric acid.

Groups 11-19 contain only eleven soils. Nearly 50 per cent. are not deficient. We draw the following conclusions, subject to modification, when a larger number of soils are studied:

Soils containing from 100 to 200 parts per million of active phosphoric acid are possibly deficient in phosphoric acid, the chances being even that they are, or are not.

Group 32-42 contains only six soils. Such soils are likely *not* to be deficient in phosphoric acid, but

this conclusion is likewise subject to modification from further study.

#### PHOSPHORIC ACID REMOVED.

We determined the phosphoric acid removed by the crops in a number of our pot experiments.

Assuming that 40 bushels of corn require 25 pounds of phosphoric acid, and a weight of 2,000,000 pounds of soil to the acre, we have calculated the number of bushels of corn which would be produced by the phosphoric acid withdrawn from the soil. One bushel of corn we estimate to require 0.00156 gram phosphoric acid per pot of 5,000 grams of soil.

A summary of the results of these calculations are presented in Table II. We find that the average possible corn crop increases regularly with each group, the only exception being groups 9 and 10, containing three soils and three crops. Right here we must call attention to the fact that these crops were grown under diverse conditions, and the climatic conditions were sometimes not favorable to the crop. But we feel that the relation between the average corn possibility and the quantity of active phosphoric acid in the soil is very significant.

The first two groups of soils, which are highly deficient in phosphoric acid, have an average possibility of 4.5 and 12.5 bushels of corn, respectively. Groups 3 to 10, the soils of which are prevalently deficient in phosphoric acid, as we have pointed out, have an average corn possibility of 19.7 to 26.5 bushels of corn per acre—the variation is not large.

Groups 11-19 and 32-42 have an average corn possibility of 50-60 bushels per acre. A soil may be highly productive, and yet appear deficient in a pot experiment.

If we consider the *maximum* corn possibility within the groups, we find that, like the average corn possibility, it increases with the quantity of phosphoric acid extracted from the soil by N/5 nitric acid, with the exceptions of groups 9-10 and 11-19. We find a maximum possibility of 31 bushels in group 2, from 37 to 59 in groups 3-10, and from 94-101 in groups 11-42.

TABLE II.—AVERAGE CORN POSSIBILITY AND AVAILABILITY OF PHOSPHORIC ACID.

Group.	Soils.	Crops.	Corn equivalent (bu. per acre).		Availability percentage.	
			Average.	Maximum.	Average.	Maximum.
1.....	9	11	4.5	9	27.0	43
2.....	13	13	12.5	31	28.8	87
3.....	6	6	20.8	36	31.2	52
4.....	6	7	19.7	37	18.4	39
5 and 6.....	6	6	24.4	42	14.4	25
7 and 8.....	13	13	26.5	59	11.7	28
9 and 10.....	3	3	22.0	39	7.9	13
11 to 19.....	4	5	52.5	101	11.1	25
32 to 42.....	5	6	60.7	94	4.7	7

It appears that soils may provide sufficient phosphoric acid for large crops, and yet respond to applications of phosphatic fertilizers. The response may,

however, vary with climatic conditions. The application of pot experiments to field conditions is a matter which we shall study.

#### AVAILABILITY OF ACTIVE PHOSPHORIC ACID.

Assuming that the phosphoric acid removed by the crop comes from the phosphoric acid extracted by N/5 nitric acid, we can calculate the percentage of phosphoric acid taken up by the crops from the data we have secured. A summary of the results of such calculation is presented in Table II. We term the percentage of the active phosphoric acid taken up by the crop, its availability. We do not wish to say, however, that the phosphoric acid taken up may not come from sources other than that soluble in N/5 nitric acid.

Considering first the average availability, we find it rises from 27 to 31.2 in the first three groups. This rise, however, is of little significance—we can almost say that the average availability is the same for the three groups.

If the phosphoric acid dissolved by N/5 nitric acid comes from the natural phosphates of lime, we cannot expect them to have a high availability. An average availability of 27.31 per cent. for the phosphoric acid of the first three groups must lead to the conclusion that some of the phosphoric acid taken from the soil comes from other sources than that soluble in N/5 nitric acid. In other words, the assumption we started with is not justified, at least in these three groups of soils.

In the first group of soils, those containing less than ten parts per million of active phosphoric acid probably do not contain any phosphate of lime at all. The 7-10 parts per million of phosphoric acid dissolved represents the solution of a portion of some highly insoluble phosphates. The availability of the phosphates based upon the portion dissolved is thus incorrect.

The availability should be based upon the total quantity of the insoluble phosphate, which is not known.

The considerations which apply to group 1 also apply to the other groups, their importance decreasing with the grade of the group. In other words, some of the phosphoric acid withdrawn by crops comes from the less soluble phosphates. It is, of course, possible that other phosphates of importance may be present in the soil. This is apparent when we consider the high maximum availability of the active phosphoric acid in the different groups.

While not decreasing regularly, the percentage availability decreases with the grade of the group. This decrease may be because the assumption is incorrect that the phosphoric acid withdrawn comes entirely from the N/5 nitric acid extracts. It is probable that the availability in the higher groups

represents more nearly the availability of the active phosphoric acid than that in the lower groups.

This matter of the availability of the phosphoric acid of the soil is being subjected to further study.

#### SUMMARY AND CONCLUSIONS.

1. Soils containing 20 parts per million or less of active phosphoric acid are highly deficient in pot experiments.
2. Soils containing from 30 to 100 parts per million of active phosphoric acid are deficient, as a rule, in pot experiments, and the extent of their deficiency is related to the quantity of active phosphoric acid in them.
3. Soils containing 100 to 300 parts per million of active phosphoric acid may or may not prove deficient in pot tests, the chances being even.
4. The quantity of phosphoric acid removed by the crop grown in our pot experiments is on an average closely related to the quantity of active phosphoric acid.
5. The phosphoric acid removed from the soil by the crop comes from other sources in addition to the active phosphoric acid.

## REVIEWS.

### RECENT PROGRESS AMONG MEDICINAL SYNTHETICS.

By V. COBENTZ.

The multiplication of medicinal synthetics during the last year has been less marked than previous periods, much to the relief of the already overburdened therapists. During the fruitful period of synthetics, which marked the discovery of phenacetin, aspirin, heroin, eucaïne, etc., the market was fairly overrun with all sorts of combinations serving as succedaneums; then followed a veritable avalanche of proprietary mixtures which threw the medical fraternity into a state of hopeless confusion. Adding to this condition of affairs, many of the latter class adopted titles of astonishing similarity with the legitimate synthetics. For illustration, what is the apothecary to dispense, when with the often illegible writing of the physician, distinctions must be made between Chinosol, Chinoro, and Chinozal; Jecoral, Jecorol and Jecoval; Thiodin or Thiolin, and so on? Also how is he to financially cope with this growing family? During the last three years the atmosphere has cleared somewhat through the aid of European State Boards of Health and the Council of Medicine and Pharmacy, who have established clear distinctions between true synthetics, medicinal combinations and the quack nostrums. The physician is now able to distinguish the real from the imitation.

#### Antipyretics.

Since the field of the p. phenetidin derivatives has produced nothing new or even offered any improvement over phenacetin, attention has been directed to the pyrazolon nucleus with the hope of securing some new combinations which might offer possible advantages over phenacetin or antipyrin. As is well known, (4) amidoantipyrin is less toxic than antipyrin, hence, as might be anticipated, pyramidon, a dimethyl (4) antipyrin, has proved itself to be a very successful and safe succedaneum, also more potent because of the presence of 2 more methyl groups. Knoll & Co. return to the base (4) amido antipyrin and patent its valeryl derivative under the name of *Neopyrin*. This prod-



uct fuses at  $203^{\circ}$ , and, according to experiments, is less toxic than antipyrin, causing no change of the hemoglobin into methemoglobin. It is also rapid in its action. As a substitute for antipyrin-caffeine migraine powder, which has been withdrawn from the markets abroad, the J. O. Riedel Co. introduce Astrolin, a compound of methylglycolic acid (38.5 per cent.) and antipyrin (61.5 per cent.), similar to salipyrin (salicylate of antipyrin).

#### Antiseptics and Disinfectants.

No class of antiseptics has established itself more thoroughly and with general satisfaction than the organic and colloidal silver combinations. Among the former class, Argonin (casein silver) and Protargol (protein silver) are popular prototypes. The new addition belongs to the latter class, being a combination of colloidal silver with albumoses, a soluble crystalline substance known as *Syrgol* (Chem. fab. Siegfried Co., Switz.).

Under this heading may be included a new mercurial, Asurol (Elberfelder Farbenfab.). Various combinations have been devised in order to overcome the caustic, irritant and albumin-coagulating action of mercuric chloride when employed either locally or subcutaneously. Among the many organic salts proposed, the salicylate is the best, but can only be used, in intramuscular injections, when dissolved in liquid petrolatum. Asurol fulfils all possible objectionable features in being readily soluble, can be given in large doses, no local inflammation, and does not coagulate albumin. This compound is a double salt of mercury salicylate and amido-oxyisobutyrate of sodium containing 40.3 per cent. of mercury.

#### Sedatives.

Valerian and its preparations have always been highly prized as sedatives. Under the belief that valeric acid (isovaleric) reduced reflex excitability, several preparations have been introduced and enjoyed considerable popularity, among which are Valeryl (valeryl diethyl amid),  $C_4H_9CO.N(C_2H_5)_2$ , and Volidol (valeryl menthol ester),  $C_{10}H_{19}O.CO.C_{10}H_{17}$ . It has since been demonstrated that the medicinal virtues of valerian rhizome reside more in the borneol than in the valeric acid. With this in view, Borneyal, valeryl borneol ester ( $C_{16}H_{25}O.C_4H_9O$ ) was introduced, but with little success. Recently an improvement has been made in selecting isovaleric acid, which is present in the rhizome, and combining it as an isoborneol ester under the name of *Gynoval*.

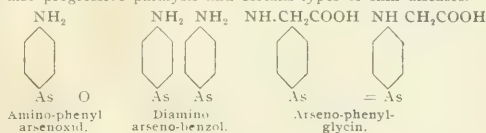
#### Arsenicals.

During recent years a wide field has been opened to arsenical therapy, which, up to this time, has been more or less limited, owing to the objectionable secondary actions attending the administration of arsenious acid. In the search for a less toxic ideal arsenical, recourse was had to the methyl derivatives of arsenious acid, oldest among these were cacodylic acid (dimethyl arsenious acid) and Arrhenol, di-sodium-mono-methyl arsenate,  $O = As(CH_3)(ONa)_2 + 6H_2O$ . In these preparations, the arsenic is so firmly linked that only a very small percentage is split off in the organism. For example, 1 gram of sodium cacodylate (66 per cent.  $As_2O_3$ ) can be readily taken and tolerated. The therapeutic value of arsenic in this form, in treatment of all diseases arising from disturbances of the nutrition, as well as a great variety of other diseases, stimulated research. A number of alkyl as well as aromatic groups have been tried by substituting one or more hydroxyls of arsenic acid with the hope of finding derivatives of valuable therapeutic properties and only one or two have found acceptance.

The mono-phenyl arsenic acid was found to be less toxic than the diphenyl arsenic acid and still less toxic is the amido derivative of the former, the sodium salt of which is known as atoxyl,  $C_6H_5(NH_2).(AsO.OH.ONa) + 3H_2O$ , which has been the center of attraction since Robt. Koch began the study of trypanosomiasis. Owing to the very stable nature of this

arsenical, 50 times as much arsenic can be administered as is permissible in the form of Fowler's solution. While varied success has attended the use of atoxyl in "sleeping sickness," it has become an accepted remedy in pellagra, syphilis, malaria, skin diseases, etc. Less uncertain and toxic, because of greater molecular stability, is Arsacetin, an arsenical built on the atoxyl type. This is the sodium salt of acetylated-para-amino-phenyl-arsenic acid, that is an acetylated atoxyl,  $C_6H_4(NH.CH_3.CO).(AsO.OH.ONa)$ . The stability in the human organism, of this anilid, may be compared to other acid anilids (acetanilid, benzanilid) which undergo a very slow splitting up in the system producing a minimum arsenical effect.

Arsacetin is 3 to 5 times less toxic than atoxyl, while its power of destroying trypanosomes appears to be greater. The peculiarity that atoxyl failed to destroy trypanosomes in laboratory experiments, while the contrary has been demonstrated in its administration, led Ehrlich to study the action of this remedy in the organism. He found that arsenic acid was reduced to arsenious, consequently the reduction products of arsanilic acid were studied, namely, *p*-amino-phenyl-arsenoxid and di-amino-arseno-benzol. These possessed a marked bactericidal action, while their relative toxicity rendered them unfit for therapeutic use. A relatively non-toxic product was found in *Arsenophenylglycin*, a reduction product of *p*-glycin-phenyl-arsenic acid. The sodium salt of the former is now marketed by the Hoechst Fabrik as a remedy for the "sleeping" sickness, also progressive paralysis and certain types of skin diseases.



## ADDRESSES.

### AN OUTLINE OF THE LEATHER INDUSTRY.<sup>1</sup>

BY ALLEN ROGERS.<sup>2</sup>

Received June 3, 1910.

When the pelts of animals are allowed to remain moist they soon putrefy and decay, while if dried they become hard and horny. To obviate these conditions, certain processes known as tanning are employed. The object of this treatment is to convert the putrescible animal matter into a material which is permanent, and at the same time possessing sufficient softness or flexibility for the purpose for which it is intended. As these range from heavy sole leather to light kid there are wide divergences, therefore, in the processes employed, materials used, and the method of their application.

The skins of various animals appear, at first glance, to have very little in common; on closer examination, however, it will be seen that they all have a general structure, thus a description of one will apply almost equally well to all others. It consists of two principal layers, the epidermis and the corium. The epidermis is very thin as compared with the true skin or corium which it covers and is entirely removed preparatory to tanning. Ordinarily the corium or true skin is the only portion which is used in the production of leather, and in order to obtain it in a suitable condition for the various tanning processes, the hair or wool, together with the epidermis, must be completely removed without damaging the skin itself; and especially, great care must be taken that the grain, or portion next the epidermis, does not suffer any injury during the treatment.

The pelts of animals come to the tanner in three conditions:

<sup>1</sup> Symposium on Leather, New York Section, American Chemical Society, April 8, 1910.

<sup>2</sup> Pratt Institute, Brooklyn, N. Y.

as green (fresh from the animal), salted (where salt has been rubbed on the flesh side), or dried (usually stretched on boards in the sun). The pelts so received are divided according to their size into three general classes, namely: *Hides*, comprising the skins from large and fully grown animals such as the cow, horse, camel, walrus and other large animals; these form thick, heavy leather, used for shoe soles, machinery belting, and other purposes where stiffness and strength, combined with great wearing qualities, are necessary. They are also cut into splits for use as shoe uppers, bag and case leathers, automobile and carriage tops, furniture and upholstery. *Kips*, the skins of undersized animals of the above species, are used for shoe leather and for a number of other purposes. *Skins*, the covering of small animals such as calves, sheep and goat, are employed for a large variety of purposes, such as uppers for shoes, pocket-books, book-binding, gloves and fancy leather.

Whether the skins are green, salted, or dried, they must first be soaked in water in order to remove the blood, dirt and salt, and in the case of dried skins to bring them to a soft condition. It is very essential that the skins should be free from all of this foreign matter before entering the limes or other unhairing solution, as the presence of salt retards the plumping, and albuminous matter is apt to set up an undesirable fermentation in the after-treatments. The time of soaking varies from one or two days to several weeks, depending upon the thickness of the hide and the age and temperature of the soak. Putrid soaks soften quicker than fresh ones, but great care is necessary in using them lest the decomposition attack the hide fiber itself. For heavy hides, which soften very slowly, it is found advantageous to run in a drum for a short time with water at a temperature of about 40° F., the tumbling movement thus materially aiding in the softening process. Following the soaking operation comes the removal of the hair, which process is known as depilation. This is necessary in all kinds of leather except that used for furs. The earliest method for accomplishing this result was by means of incipient putrefaction, in which case the soft mucous matter of the epidermis became affected, thus causing hair to become loosened without materially injuring the true skin. This method is still employed by many tanners of sole leather and is called "sweating." The operation is conducted in closed rooms which are kept at a temperature of about 70° F. The hides are hung in small chambers ("sweat pits") holding about 100 hides each. After four to six days of this treatment the hair is sufficiently loosened to be removed by working over a rounded beam with a blunt knife made for the purpose. No matter how carefully this operation may be conducted there is liability, however, that the putrefaction attacks the skin itself, thus causing a weak grain, and for this reason we find it being used less and less.

A depilating agent which works very satisfactorily is lime, and it is the agent which is almost universally employed. Although it has its disadvantages, its good points far outweigh those of any other substance. In preparing the lime for this operation a quantity of fresh lime, calcium oxide, is slaked by placing it in a shallow tank, similar to that used by builders, and sufficient water added to thoroughly moisten it. At the end of one or two hours it becomes heated and falls to a powder, and is then mixed with enough water to form a thick paste. In this condition it may be kept for weeks, or even months, without any material change. When required for use a sufficient amount is dug out, stirred with water to remove rocks, and then run into the pits. As only the lime in solution is available for unhairing it will be seen that the addition of a large excess is unnecessary, it being essential simply to provide a surplus of solid lime to replace that taken up by the hide. The usual method of liming is to lay the hides one at a time in the lime solution, taking care that each hide is well immersed be-

fore entering the next one. The hides are taken out each day ("hailed") and the liquor well plunged up in order to distribute the undissolved lime throughout the pit. They are then thrown back ("set"), care being taken to see that they are fully spread out. In some tanneries the hides are joined by hooks and reeled from one pit to another or to the same pit. It is sometimes customary to suspend the hides in the solution, and by means of a paddle keep the limes in motion.

The action of lime on the hide is to swell up and soften the epidermis cells, dissolve the mucous layer and loosen the hair so that it may be scraped off with a blunt knife. The actions on the true skin is also very vigorous, causing the hide to become plump and swollen, at the same time dissolving the cementing material of the fibers, thus causing them to split up into finer fibrils. The swelling is probably due to the formation of a lime soap, caused by the union of the lime with the fatty matter of the hide.

The time of liming varies with the season of the year, and with the kind of skins being treated, the time being from three to fifteen days. The age of a lime also has a great influence on the time of treatment as well as on the character of the finished product. As old limes unhair much quicker than fresh ones it is often customary to place the hides in an old lime for several days, or until the hair and epidermis have started to loosen, then change them to a fresh lime, which produces the necessary plumping of the fiber. Great care, however, must be taken that the limes do not become too old, as this condition will be very apt, especially in hot weather, to produce a transparent swelling of the goods, with destruction of the fiber.

Other depilating agents are sometimes employed, either alone or in conjunction with lime. The red sulphide of arsenic is one of commonly used substances, and in connection with lime is very beneficial in the case of fine leathers, to which it gives the necessary stretch, softness, and clearness of grain, without the loss of hide substance and loosening effect caused by ordinary liming. The amount varies somewhat, but may be said to run from 0.1 to 0.4 per cent. of realgar and 4 to 6 per cent. of lime, reckoned on the weight of the green skins.

When sodium sulphide is employed in strong solutions, say 5 per cent. and over, it has the effect of very rapidly reducing the hair and epidermis to a sort of pulp, which may be easily swept off with a broom, or even washed off in the drum. The operation is usually conducted in a paddle, taking about two hours for the complete removal of the hair and epidermis. The action on the hide substance, and especially the cementing material, is very slight, although the grain is swollen and temporarily rendered somewhat tender. As this strong solution destroys the hair it is only used on such stock as goat or horse where the hair is of minor importance. On the other hand, when used in weak solutions, say 0.25 per cent. and less, in conjunction with lime, the hair is but little injured, the hair-roots and dirt being rapidly loosened, with a result somewhat similar to that produced by arsenic sulphide.

When the process of depilation is completed the skins are removed from the pits and allowed to drain for an hour or so. They are then placed on the beam and the hair removed as described under the sweating process. In recent years various machines have been devised to accomplish the removal of the hair, although many tanners still prefer to keep to the older hand method.

After being unhaird the skins are "fleshed," which operation is for the purpose of removing any fat or flesh that has been left on the pelt by the butcher. The fleshing may be accomplished on the beam in a somewhat similar manner as that described for unhairing, except that the knife employed is heavier and sharp on both sides. In nearly all modern tanneries, however, the beam has been discarded, as machines for the purpose have taken its place.

It is very essential that the lime, or other depilating agent, should be completely removed when it has done its work, since its action is very harmful when brought into contact with tanning materials. For most leather, also, it is not only necessary that the lime be completely removed, but that the skin should be brought from its swollen to a soft and open condition. To accomplish this result on the heavier classes of dressing leather, such as split hides, kips, colt, and calf skins the stock is run in a weak fermenting infusion of pigeon or hen manure, the time depending upon the strength of the liquor, and upon the nature of the goods under treatment, the process being known as "bating." "Puering" is a very similar process, applied to the lighter and finer skins, such as glove-kid and moroccos, in which dog manure is substituted for that of birds. As the mixture is used warm and the skins are thin, the process is complete in a few hours. Neither bating or puering are very effective in removing lime, but seem to act by means of bacterial products upon the hide substance, thus causing the pelt to fall, that is, to become soft and flaccid.

Following the bating, and sometimes taking its place, comes the "drenching" operation, the purpose of which is to remove the last traces of lime and to slightly plump the skins. The drench liquor is prepared by allowing an infusion of bran in warm water to ferment under the action of special bacteria which develop lactic and acetic acids.

The method of deliming just mentioned, although it presents many difficulties and is uncertain in its action, is very largely used, notwithstanding the fact that many substances have been put on the market to replace it. But as the other papers of the evening will take up this subject we will not consider them at this time.

Having passed through all of the processes mentioned above, the hide or skin is now in the proper condition for the actual tanning operation, which may be conducted by any one of several different methods. As my time is limited, however, it will perhaps be best to mention only briefly the various processes, as they will be discussed more in detail by those who have papers on the special topics.

The oldest method in vogue is that known as "oil tannage," which consists in treating the hide or skin with a mixture of fish and other oil in a machine which works the skin by a sort of kneading motion known as the "stocks." During this operation heat is developed, resulting in the formation of aldehydes and other oxidation products. The excess of oil is removed by scraping and pressing, the product obtained being known as "dégras." The skins are then washed with a fairly strong alkaline solution, the alkaline solution neutralized with an acid with the result that fatty acids are produced known as "sod oil." This method of tannage is used especially for the so-called "chamois" leather.

For the manufacture of white and light colored leather it is usually customary to employ an "alum tannage." This method consists in treating the skins with a mixture of sulphate of aluminium, salt, flour, egg yolk and olive oil. This treatment produces a hard "crust" in which the skins are allowed to remain for quite a length of time, after which they are softened, sized and finished.

The most important method of tanning is that in which a vegetable material is employed, the results obtained being due to the presence of tannic acid. The operation consists in placing the skins in a dilute solution of the tanning material, such as quebracho extract, and gradually increasing the strength of the liquor until the treatment is completed. On removing from the tanning solution the skins are washed, dried, softened, colored, seasoned and finished as desired.

A recent process, and one which is meeting with increased application, is that known as "chrome tannage." The Schultz process was the first to meet with any commercial application

and consists in saturating the skin with a solution of dichromate of sodium or potassium together with hydrochloric acid. The chromic acid thus produced is absorbed by the hide substance, and is finally reduced to the chromic hydroxide condition by means of sodium thiosulphate and hydrochloric acid. A second process, brought to perfection by Martin Dennis, consists in treating the skin with a basic sulphate of chromium. The latter method has the advantage over the former in that it is more easily controlled and less expensive in its operation.

Within the past few years formaldehyde has been introduced as a tanning material and bids fair to open up a new field for the production of leather by chemical means.

As my part in the program of the evening was to pave the way for the other speakers, I will draw my remarks to a close, leaving the more detailed description of tanning, coloring and finishing for those who are better able to handle the respective subjects.

## THE SMOKE PROBLEM AND THE COMMUNITY.<sup>1</sup>

By CHARLES BASKERVILLE

The problem of smoke abatement has been a vital one for many centuries. Some six hundred years ago, the citizens of London petitioned King Edward I to prohibit the use of "sea coal." He replied by making its use punishable by death. This stringent measure was repealed, however, but there was again considerable complaint in Queen Elizabeth's reign, and the nuisance created by coal smoke seems to have been definitely recognized at this period. Since this time there has been continual agitation, together with much legislation, both abroad and in this country. In the seventeenth century, King Charles II adopted repressive measures in London, and in the present century anti-smoke crusades have been frequent. In fact, the smoke problem will undoubtedly continue to demand attention until it is either entirely solved by the abolishment of the use of solid fuel or by the installation of devices and methods which shall prevent the formation of smoke in furnaces, regardless of the nature of the fuel.

It has been suggested that the production of fuel gas at the collieries, and its transmission to the various centers for combustion, will solve the problem by elimination. However, we are at present dependent upon local installations for the minimization of this unnecessary evil, but a realization of numerous rational changes in methods of generating heat and power is necessarily near at hand.

At the conference on smoke abatement held in London in 1905, Lodge suggested two methods for smoke abatement: the burning of coal at the mines to produce gas or electricity for transmission to cities, and the electrification of the air on a large scale. The latter suggestion cannot be given attention on account of the expense that would be entailed, although it has received favorable consideration by some.<sup>2</sup>

Good firing is admittedly an important factor in smoke prevention, and it has even been regarded as the main factor of the problem,<sup>3</sup> but it would appear that most authorities favor the distribution of gas as a means of at least alleviating the smoke nuisance.<sup>4</sup>

The economy resulting from smoke abatement is a potent argument in its favor. That this phase of the problem has

<sup>1</sup> Opening address in the symposium on "Smelter Fumes," San Francisco meeting of the American Chemical Society, 1910.

<sup>2</sup> Lord Rayleigh has a theory on dispelling smoke and fog by electricity. On the possibilities of smoke deposition by electrical means, see *J. Roy. San. Inst.*, **27**, 42; and *Elec. Rev.*, **47**, 811.

<sup>3</sup> Caborne, *J. Roy. San. Inst.*, **27**, 142.

<sup>4</sup> For example, Lodge, *Des Voeux*, A. J. Martin and A. S. E. Ackermann. In this connection, see *J. Roy. San. Inst.*, **27**, 42, 64, 80, 85.



little to do with the ethical side of the subject cannot be gained, since all communities have the right to demand its abatement regardless of economic considerations. In this connection, it is appropriate to discuss the legal status and different phases of the smoke problem, a subject which the writer has dealt with in detail elsewhere.<sup>1</sup>

Every individual has the right to have the air distributed over his properties and habitation in its natural condition, that is, free from all artificial impurities. In fact, it may be stated that no one has the right to interfere with the distribution and amount of pure air which flows over another's land any more than he has to interfere with his neighbor's soil. This right is strictly a natural one, and every use of property that causes an unwarrantable impregnation of the air with foreign substances to the detriment of another, is a nuisance, and is actionable as such. The air must be as free and pure as can be reasonably expected.

Based largely on the preceding, it is laid down broadly as a general rule in law that any act, omission or use of property which results in polluting the atmosphere with noxious or offensive gases or vapors, thereby causing material physical discomfort and annoyance to persons residing in the vicinity, or injury to their health or property, is a nuisance. This rule has been supported by decisions in Delaware, Illinois, Kentucky, Missouri, Pennsylvania, Texas, and Wisconsin.

#### WHAT CONSTITUTES A NUISANCE.

The question as to what degree of impurity imparted to the atmosphere by one in the use of his property constitutes a nuisance, is one of fact, and is determined by the jury from the circumstances of each case. Injury is, of course, a question of compound facts. No precise tests may be given that are applicable to all cases. In the consideration of the surrounding circumstances of a case, the character and nature of the gas complained of is of prime importance, and the times and periods of the generation of the gas, or the constancy and frequency of inconvenience caused, and the nature of the business, its location, management and manner of construction, must all be taken into careful consideration.

To illustrate the last condition, a manufacturing business may be a nuisance because it is located in a residential or populous part of a city or county, whereas it should be located in a more remote locality; or a nuisance may arise merely from the faulty construction of a plant or from the negligent or improper manner in which the business is conducted and the works kept.

Although diminution in value is the proper element of damages and in some cases the actual measure of the nuisance, yet it has been ruled in New Jersey that mere diminution of the actual or rental value of a property is not sufficient to make a business a nuisance. According to common law, a sensible injury is only a visible injury, and in general it may be stated that injuries must not be dependent upon scientific tests to discover. Theoretical injuries furnish no ground for abatement, and an injury to property must be irreparable to cause a court of equity to interfere to abate.

#### VARIOUS STATE DECISIONS.

It has been ruled in Connecticut that a manufactory which produces such unwholesome odors that the workmen of a neighboring manufactory are prevented from working therein, is a nuisance; and it has been given as a decision in Iowa, Kentucky, Massachusetts, New York, Texas, and Vermont, that a noxious trade may be a nuisance even in a remote locality, providing it is located near a public highway and inflicts serious discomfort on people passing by. However, it has been ruled in Tennessee that such odors or gases must be really dangerous to public health and not merely offensive to certain individuals.

Odors which are carried a great distance by the wind and

which are "unpleasant and objectionable," according to a decision handed down in North Carolina, is not sufficient ground for the interference of a court. Odors or gases must work some substantial annoyance or some material physical discomfort to maintain an action; this point is well supported by precedents. It has been decided in South Carolina that where the plaintiff has sustained injury from the escape of noxious gases from the defendant's factory and also injury from other causes, the defendant is not relieved from liability for the injury he has caused.

Dust, smoke and cinders, even when accompanied by noxious gases, are not nuisances *per se*, but amount to nuisances, whether accompanied by noxious gases or not, if they cause injury to neighboring property to such an extent that its value is diminished, or if they so pollute the air as to cause inconvenience materially interfering with physical comfort and the enjoyment of the property (California, Connecticut, Illinois, Indiana, Kentucky, Maryland, Massachusetts, Missouri, New Jersey, New York, North Carolina, Ohio, Pennsylvania and Tennessee). If smoke and its accompanying gases cause sickness or injury to health, an action for damages lies, even though the fuel producing the nuisance is necessarily used.

#### A DUCKTOWN SUIT.

In the suit of the Ducktown Sulphur, Copper and Iron Company *vs.* Barnes, *et al.*, where smoke and noxious gases from a smelting works injured the property and endangered the health of the adjoining land-owners, the action for damages lay, even though the business was being carried on in a suitable locality, with the most improved appliances, and furnished employment to nearly the whole community. It was decided that it is no defense to an action for damages that there were similar establishments in the neighborhood before the plaintiff moved there, and that it is no defense that the works could not be operated without giving rise to noxious vapors. It was decided that the owner was entitled to recover all the damages sustained without reference to the incidental benefits or advantages to the land by reason of the market it afforded for timber and garden products.

The decision in the preceding would seem to indicate that no prescription can be pleaded for a nuisance, and that neither its collateral benefit to the community, nor the good intent of the projector is a defense. It would appear that it is alone sufficient to sustain a conviction that the comfort of the community is impaired. However, the findings in some cases in Montana in part conflict with aforesaid decisions and stand out in sharp contrast.

#### SOME MONTANA DECISIONS.

In the suit of Hugo Magone *vs.* The Colorado Smelting and Mining Company, *et al.*, in which the plaintiff sought \$20,000 damages and a permanent injunction for alleged damage to his land and crops through the action of tailings and tailings waters, the prosecution attempted to demonstrate the cause of the damage by chemical analyses. The defense was based on the fact that the water carried mere traces of possible poisonous salts in solution, and that the soil, which was poor black alkali in nature, was not properly irrigated. Although damages amounting to \$1700 were awarded the plaintiff, the injunction was refused on the principle of the "greatest good to the greatest number."

One of the most extensive suits ever heard was the one brought by F. J. Bliss *vs.* The Anaconda Copper Mining Company and Washoe Copper Mining Company. This suit involved the question of fumes, and was brought for a perpetual injunction. During the case it was brought out that the Anaconda Company pays more than half the taxes of Deer Lodge County, where its smelter is located; about one-third of the taxes of Silver Bow County, where its mines are located; and with asso-

ciated companies they are the principal tax-payers in nearly every part of Montana. It was shown that the company had erected a stack 300 feet high and that, before the erection of this stack, when they used several smaller stacks, claims for about \$340,000 were settled.

The injunction was refused for the same reason as in the preceding case. The amount of damages fixed by the master in chancery was small. A further hearing in the case was ordered to ascertain if there is not some means of reducing the amount of arsenic in the flue dust, in order that a specific rule may be made which will afford relief.

#### THE CONTRA COSTA CASE

In Contra Costa County, California, where an ordinance was passed to regulate the distribution of noxious gases by smelting plants, the board of supervisors of the county granted the companies involved 60 days' time to instal apparatus and appliances to prevent the nuisance. County ordinances of a similar nature may yet solve the problem in affected parts of the country, especially in the Western States. City ordinances usually afford little relief.

The doctrine that an industry or business erected in the vicinity of similar establishments could not become a nuisance in that locality, or that any exceptions should be made in favor of a business lawful in itself and useful in its results, that is otherwise clearly a nuisance, excepting for the fact of location and usefulness, is generally considered to stand out of the pale of recognition of modern authority and to be entitled to no weight outside of Pennsylvania. However, some jurists, particularly in the western smelting districts where a broader view must necessarily be given to the matter, have rendered decisions which would seem to be contrary to this general rule.

#### OTHER LOCALITY CONSIDERATIONS.

In the case of *Dittmann vs. Repp*, the Supreme Court of Maryland held that in determining the question of nuisance from smoke or noxious vapors, reference must always be had to the locality. For instance, a party dwelling in a city in the midst of crowded commercial and manufacturing activities, cannot claim the same quiet and freedom from annoyance that he might rightfully claim in the country. When the population moves up to a nuisance which was previously in solitude, then, as a general rule, the nuisance must recede. It must, however, be reasonably offensive.

On its first introduction, gas was declared to be deleterious to the health of the community, and in some localities steam railways were at one time so offensive to particular local authorities that attempts to prosecute them as nuisances were not infrequent. Grievances of prosecutors in such cases as pertain to damaging gases in particular are often sentimental or speculative—just as they were at the time when the use of gas as a fuel was regarded as a nuisance—without due regard to the substantiality of the "nuisance."

#### POPULAR MISCONCEPTIONS.

Persons engaged in agricultural pursuits in manufacturing districts invariably have impressions of the destructive action of the waste gases resulting from fuel combustion, etc., upon vegetation, but these are generally founded on observation and tradition. There are many instances of sympathetic juries having fostered these impressions, basing their awards on miscellaneous general evidence and not upon scientific examination. In such cases, too much reliance is often placed on the appearance of individual trees and of isolated trees.

In some cases, the injury through atmospheric influence resembles smoke injury. A lack of iron and the ravages of insects produce yellow or red blotches on flora leaves. A distinction from fume poisoning can be discovered, however, by transverse sections under the microscope, when mycelium strings will be observed between the cells. In the case of pines,

stronger trees absorb less than the weaker ones, and even though there is no visible injury, as observed in the change in the appearance of the needles, a microscopical examination will demonstrate that the chlorophyll substance has undergone changes or destruction when treated or exposed to sufficiently concentrated sulphur dioxide or hydrogen chloride.

Poor soil, exposure of wind, especially dry wind, diminished water supply, and fungi, all produce morphological conditions in vegetation which lead to the gravest misapprehensions in the minds of rural folk, and oftentimes accusation of fumes and gases as the cause results, either wrongfully or on *à priori* grounds. Ordinary testimony based upon odor alone should, as a rule, carry little weight.

It is well known that the present sociological and political ideas which obtain in the rural communities, and certain abuses of the centralization of capital on the part of corporations, have resulted in injuring the chances of the latter in suits of this nature. While it is true that certain corporations conceal their processes of manufacture, the nature and amount of materials used and the output of product, as well as employ other precautions in order to render the recognition of damage done by fumes more difficult, yet many instances are known where gardens are purposely set out with expensive flowers unsuited to the climate, just to profit by the damage for destruction by "noxious gases," and manufacturers are not protected from such malicious actions.

#### EXPERT BOARD TO ASSESS DAMAGES.

Some time since I made the suggestion with the aim of justice in mind, that complaints of this nature be settled by a commission composed of three experts in such matters, one being selected by each of the parties and the third being chosen by these two; or two of the experts may be appointed by the court, and a third selected by these two. Such a board of experts could investigate the facts of the case scientifically on the spot, and, if damage has been done, fix the amount and warn the offenders that a recurrence will bring forth more severe penalties. Negligence on the part of the manufacturers would cease, as well as annoying and expensive interruptions of business. I am convinced, and I have reasons for making the statement, that honest manufacturers would welcome such a change. It is recognized that such settlements would not be looked upon with particular favor by the legal fraternity, but is interesting to note that a recent case brought against the Mammoth Copper Company, in Shasta County, California, was settled by an arbitration board composed of three horticulturists, both parties to the suit having agreed to abide by their decision.

In this connection it may also be remarked for the benefit of those who have not had occasion to investigate the matter, that there is neither entire uniformity nor definiteness of statement in the codes of our several states in regard to the contamination of the air or the pollution of streams. When such contamination becomes wretchedly bad from any cause whatever, protests sometimes check the wrong and secure legislation. The continued pressure of unsubsidized publicity often encourages direct action in these matters.

#### CASES OF FEDERAL JURISDICTION.

When a manufactory in New Jersey generates gases which are complained of in New York or when smelter fumes produced in Montana or Tennessee affect the vegetation in a neighboring state, it becomes a Federal matter. In the latter case, we have also the same indefiniteness of statement in our laws.

Several rules based upon precedents and not specified regulations obtain, the rule of action is not clear, and there is a tendency toward a too technical construction of the law. Some have asserted that there is no need for legislation until there is a demand for it, but the law of equity is not the outcome of

specific needs and abuses of justice, and is rather contingent upon anticipated conditions; and manufacturers, as well as citizens, desire just protection. As in criminal law, it is to be deplored that cases may be lost in lower courts on judicial rulings which, in other similar cases, are afterward reversed by higher courts.

A Federal decision of great import was handed down in the case of the State of Georgia *vs.* The Tennessee Copper Company and the Ducktown Sulphur, Copper and Iron Company. The United States Supreme Court held that a state has the right to protect its forests and that a company can be enjoined for operating its smelting works in such a manner as to cause damage to property in a neighboring state. It was held that a state has the right to protect its citizens when their property is subject to damage by operations in another state.

The interest involved in the United States is sufficiently great and distributed to make it appear advisable for the Department of Agriculture to extend its operations and investigations in this field, co-operate with the similar departments in the states, formulate reasonable legislation, and recommend the enactment of a uniform and definite law. In such an event the government officials would undoubtedly receive the cordial support and encouragement of the owners of the industry, perhaps even financial complimentary support. Such has been the case in England, where there is in force a law defining what amounts of waste gases may be permitted in the air.

#### FOREIGN LEGISLATION.

A brief discussion of the foreign laws of importance may not be out of place in this connection. According to Lord Derby's alkali act, the sulphate works of England were not permitted to discharge more than 5 per cent. of the hydrogen chloride gas produced. This clause was later altered to forbid more than 0.464 gram of HCl per m<sup>3</sup>. With regard to the sulphuric anhydride, the Alkali Works Amendment bill of 1901 prohibits the discharge of more than 4 grains of SO<sub>3</sub> per ft<sup>3</sup>. of residual gas. The result of these laws has been a notable diminution of the amount of acid gases allowed to escape from works—a result not achieved by numerous prosecutions.

Until the beginning of 1907, the lead and copper smelting works in Great Britain were at liberty to discharge their fumes into the air as long as no objections were raised by persons near-by. Now these smelters are included in the new alkali works regulation bill. However, the method of dealing with the existing smelting works is left somewhat elastic by the act. Contrary to the American law, the gaseous output could not be restrained up to 1907 if the population moved up to the works. This is exemplified by the history of Swansea, Wales. In Prussia, in the granting of concessions for new works it is enacted that the amount of sulphuric anhydride in the waste gases should not exceed 5 grams in one cubic meter.

#### IS A UNIFORM FEDERAL LAW IMPRACTICABLE?

An objection which has been urged against the regulation of the amounts of acid gases discharged into the air is this, that it is not practicable to establish a permissible amount of noxious gas which may be emitted for all parts of a country owing to geographical and meteorological conditions. This is indeed well founded.

Other important questions to be considered in the formulation of a Federal law, such as referred to, are the enforced selection of location for smelting works, etc., preferably on plains or level portions of the country with due regard to winds, and the advisability of enforcing the adoption of tall stacks and chimneys by all works generating noxious gases. In regard to the first, it has been suggested that smelting companies be given the right to condemn land within a certain radius of their works, especially if they were located before the advent of a definite number of people. Such a bill passed the legislature

of Utah but was vetoed in 1907 by Gov. J. C. Cutler on the ground that such a measure bore the marks of class legislation. The Utah bill providing for the condemning of land within a radius of four miles from a smelter in counties of less than 75,000 people.

As to the second question, the assumption that higher chimneys will diminish the amount of damage done by allowing the acid gases to become more dilute before reaching the vegetation is not realized, according to the experience of many industrial concerns. Notwithstanding the fact that unquestionable benefits are derived from dust chambers, and the contrivances associated with high stacks, and the fact that the adjacent vegetation is not so much injured from a high as from a low stack, there is considerable damage wrought by gases from high stacks, as remote vegetation is reached by smoke, etc., which would not be otherwise affected. In damp, heavy air, fumes heavier than air fall rapidly to the ground; and when the wind blows, the gases sink gradually, but hold together for considerable distances, so that no unusual dilution is effected by such means. This I have verified by experiments on a large scale.

#### THE WORK OF THE EXPERT IN THIS CONNECTION

The usual gases which give rise to complaint in manufacturing localities are the following: Chlorine, which is emitted by pottery kilns and ceramic products manufactories, and plants for the electrolysis of halides; hydrogen chloride, which is produced by the combustion of coal, and by pottery kilns, ceramic products manufactories (partly from the coal and partly from the clay), nickel and cobalt smelting, platinum refining, glass manufacture, fertilizer manufacture, the chloride of lime industry, and soda manufactories; sulphur dioxide and sulphuric acid, which result from the combustion of coal, coke, and gas, copper smelting, and from many other industrial processes; and fluorine and hydrofluoric acid, which are emitted from phosphate fertilizer and heavy chemical plants.

However, the destructive action of fumes in the vicinity of chemical works is generally due to the presence of sulphurous acid, sulphuric acid or hydrochloric acid. Since hydrochloric acid is absorbed in the same manner as sulphurous acid and sulphuric acid by the leaf organs of plants, the proof of injury may, in a measure, be established by an estimation of the chlorine content. It is usually easy to establish an abnormal chlorine content in a plant, providing, of course, that actual hydrochloric acid action is apparent. In chemical factories the investigation of suspected injuries is very much complicated owing to the fact that the combined action of sulphurous acid, sulphuric acid, and hydrochloric acid, as well as that of coal fumes, must be taken into consideration. Consequently, it is often difficult to decide how far the injury done to vegetation, especially slight injuries, is due to the acid fumes coming from manufacturing processes and the injury caused by the combustion of coal. In general, however, one does well to make himself acquainted, as far as possible, with the surrounding neighborhood and the pathological conditions. The forms of injury found furnish abundant points of distinction as to the nature of the injurious gases; and repeated local examinations and observations at different periods are advisable.

The chemical analyses should be more comprehensive than simple determinations of the abnormal sulphuric acid and chlorine content of the affected plants: If the whole investigation is to be of value, the presence of abnormal amounts of the noxious gases must be shown in the vicinity of the source of contamination at various points at different distances. An exhaustive local examination is necessary. Injury from sulphur dioxide often shows itself by the increased sulphur trioxide content of the foliage of the affected vegetation, but in order to ascertain whether the injury to vegetation is due to the action of sulphurous acid and sulphuric acid or to the ac-



tion of hydrochloric acid, it is necessary to make estimations of both in the neighborhood of the manufactory. Since rain water and dew nearly always contain sulphuric acid and chlorine (calculated as such) in small amounts, no reliable conclusion can be drawn in regard to the increase of these gases from the source of contamination, except by long-continued observations at different distances and by exact quantitative analyses.

To determine absolutely the action of hydrochloric acid on plants, it is necessary to make estimations in the gas currents and then compare them with the normal chlorine content in the vicinity, as determined by analyses made at stations at different distances and in varying weather conditions. It is important to consider the chlorine contained in the soil in the neighborhood of factories, especially when estimations of chlorine in plants are made.

#### SULPHUR DIOXIDE AS AN IMPURITY OF CITY AIR.

Sulphur dioxide has been shown to be present in considerable amounts in the air of various manufacturing cities, when the total amount and not the concentration is considered; and, since the atmosphere is the great receptacle for all gaseous emanations, it may be said in general that this gas is a common impurity of city air.

The writer sometime ago made a number of determinations of the sulphur dioxide content of the air of New York City. Stations were established throughout greater New York City, including the high office buildings, parks, subways, stations, and railroad tunnels; and very variable results, as might be expected, were obtained. The determinations may, in part, be thus summarized:

Locality.	SO <sub>2</sub> in parts per million.
Elevated portion of city, near a high stack . . .	3.14
Various parks . . . . .	0.84 (maximum: others negative).
Railroad tunnels . . . . .	8.54-31.50
Subway . . . . .	None
Downtown region . . . . .	1.05-5.60
Localities near a railroad . . . . .	1.12-8.40

In 1907, the residents of Staten Island, as well as some on Long Island, complained of the noxious nature of the air wafted over from various plants in New Jersey. This induced the Department of Health of the City of New York to investigate the air and vegetation in the vicinity of the Borough of Richmond, Staten Island, and some of the results obtained are given below by permission of the department:

Substance.	Impurity.
Air . . . . .	Trace of sulphuric acid.
Air . . . . .	0.0066 percent. SO <sub>2</sub> by weight.
Air . . . . .	Trace of sulphuric acid.
Grass (three samples) . . . . .	Sulphuric acid present.
Grass . . . . .	0.24 per cent. SO <sub>2</sub> .
Grass . . . . .	0.70 per cent. SO <sub>2</sub> .
Leaves . . . . .	0.19 per cent. SO <sub>2</sub> .
Leaves . . . . .	0.28 per cent. SO <sub>2</sub> .
Soil . . . . .	0.0015 per cent. SO <sub>2</sub> .

These results do not really give us anything definite, as the comparative factor is absent.

Sulphur dioxide to the extent of 1300 tons, calculated as 80 per cent. sulphuric acid, is discharged every twenty-four hours into the air of New York City from the combustion of coal alone. From an economic standpoint, this is an enormous, partly avoidable, waste, while from a sanitary standpoint, any disinfecting action it exerts on the organic wastes arising from the streets is greatly counterbalanced by its general injurious effects which may be thus summarized:

1. Its presence in atmospheric air is a menace to hygienic welfare, since it has serious effects on susceptible persons and particularly exerts deleterious effects upon the respiratory organs. SO<sub>2</sub> in the air of manufactories tends to produce bronchitis and anemia.

2. It exerts an injurious action on plant life. In this action it is less violent than hydrogen chloride, sulphuric acid and fluorine, but owing to its less solubility and consequent slower condensation, it has a wider distribution. In Manchester, England, in 1891, it was learned that the greatest injury to plant life is due to the emanations from dwelling-houses.

3. The condensation of sulphurous acid with moisture in fogs and hoar frosts seriously affects goods printed with colors sensitive to sulphurous acid; for example, logwood, Brazil wood shades, and aniline black.<sup>1</sup>

4. Sulphur dioxide proceeding from the combustion of coal and coal gas, the quantity of which in towns is considerable, necessarily destroys the ozone of the air. This may account for the definite variations of the proportion of ozone observed at various localities.

5. In anti-cyclonic periods the amount of sulphur dioxide rises considerably, and at such times this increase is accompanied by at least as large an increase in the amount of organic impurities in the air.

#### RECLAIMING DEVICES.

To conclude, the main solution of the "fume question" and "air pollution" would seem to be in the enforced use of waste-reclaiming devices by the enactment of a Federal law regulating the amount of waste gases to be permitted to pass into the air, but laws do not execute themselves, and strict administration, sufficient appropriations for the determination of facts, enlightenment of the public mind as to the effects of noxious industrial emanations, and civic interest would all be absolutely required for the enforcement of such a law. In England the enactment of similar laws laid the foundation of the great chloride of lime industry, and the subject has received merited attention since 1863; in fact, one might say since 1836, the year in which Gossage solved the problem of hydrochloric acid condensation.

In Germany, after extensive experiments in 1848, the furnaces in the smelting districts were remodeled and the volume of the dust chambers increased. This proved advantageous to the smelters, as the following shows: The Freiberg Smelting Works paid 55,000 marks for damage in 1864, and but 4,793 marks in 1870, after installing means of condensing the acid gases. In our own country it is encouraging to note that some manufacturers and smelters have at last begun the installation of waste recovering contrivances—surely a decided step toward the solution of a great national industrial problem, however novel and radical such devices may appear.

## NOTES AND CORRESPONDENCE.

### STANDARD SAMPLES, BUREAU OF STANDARDS, WASHINGTON.

The Bureau of Standards, Washington, D. C., is ready to distribute the following analyzed samples:

No. 6a. Iron D, replacing the original D of the American Foundrymen's Association.

No. 24. A vanadium steel with between 0.1 and 0.2 per cent. vanadium. At present only a provisional certificate of analysis can be issued with this steel.

No. 25. A manganese ore, for total manganese and available oxygen.

No. 26. "Crescent" iron ore, for alumina, lime and magnesia.

No. 27. "Sibley" iron ore, for iron, silica and phosphorus.

No. 28. "Norrie" iron ore, for manganese (low).

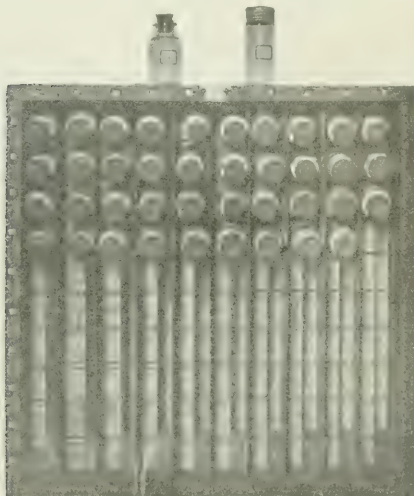
A new schedule of fees goes into effect July 1, 1910, and thereafter the only discount allowed will be ten per cent. (10%) on four or more samples, alike or different.

<sup>1</sup> Soft coal smoke interferes with the manufacture of delicate shades of silks; it has been asserted by manufacturers.

Two new circulars relating to the Bureau's standard samples have been prepared for free distribution. Of these, Circular 25 contains general information regarding all samples, and Circular 26 relates to the methods used by the Bureau chemists and many others in analyzing the above manganese and iron ores.

#### SOME LABORATORY DEVICES.

The accompanying figure pictures the writer's device for filing and handling samples contained in bottles. The frame is made of board about 2 cm. thick; its internal dimensions are 57 x 57 x 11 cm. This space is divided into one hundred equal compartments by nine vertical strips of galvanized sheet iron and nine pairs of galvanized iron wires, which pass horizontally through the strips into the frame. The bottles lie on the wires and abutt at the back against flanges which form a part of each of the strips of sheet iron. The frame is made



No. 1.—A sample file.

ridged and held in shape by suitable braces at the corners, back side. The above are the construction and dimensions of our small transportable files for bottles of 100 to 200 cc. capacity; in the case of our larger and stationary files (for jars or bottles of 800 to 1000 cc. capacity) we use a cheaper construction, namely: shelves (board) take the place of the horizontal wires, and nails—a pair fore and aft driven into the board between the bottles—take the place of the vertical strips, and keep the bottles or jars in vertical alignment.

These files, about a score of the small transportable ones and over two score of the stationary ones, have been in use in our laboratory for the past seven or eight years and are regarded as indispensable. By their aid the chemist can place his hand, without confusion or loss of time, on any particular sample among several thousand.

Observe the label "7400" at the top of the frame; it means that this file contains that particular hundred samples whose first two figures are 74, namely, Nos. 7400 to 7499, inclusive. Observe also the figures 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 on the top and left margins of the frame, beginning at the upper left-hand corner. The bottles are filed by tens, left to right; the first ten, 7400-7409, inclusive, occupy the top row; the second ten, 7410-7419, inclusive, the second row, and so on down to the

last ten, 7490-7499, inclusive, which occupy the last, or bottom, row. To find any particular sample that one might wish, say No. 7446, one goes to the file being the appropriate label, in this case "7400," runs the hand down the left-hand margin to figure "4" and thence horizontally to figure "6"—that gives the sample sought—7446.

The samples (fertilizers, feedstuffs, soils, etc.), prepared for analysis in the preparation room, are placed in the small files and carried to the weighing-room, where they are hung against the walls or set on tables near the balances. The original samples (fertilizers, for example) are returned—what is left of each—to its jar, sealed, placed in the large or stationary file for future reference, if need arise. The prepared original samples bear the same numbers.

J. M. PICKEL.

RALEIGH, N. C., June 22, 1910.

#### BOOK REVIEWS AND NOTICES.

*Les Secheries Agricoles: Etude Economique et Technique de la Desiccation des Produits Agricoles.* Par D. SIDERSKY, Ingenieur-Chimiste. Paris: Lucien Laveur, Editeur, 13 Rue des Saints-Peres (VI<sup>e</sup>).

Sidersky has written a very useful brochure on the above subjects, showing how the science of desiccation may be profitably employed for agricultural purposes.

The work is especially interesting to those who have to deal with cattle foods derived from sources where there is a very large excess of water.

Among the subjects treated in the book are: The pulps of sweetmeats, the drying of sugar beets, the drying of leaves and necks of sugar beets, the drying of potatoes, the utilization of pulp from starch factories, the drying of artichokes, of the pomace of wine, of the slops of breweries, the desiccation of milk and of the products of the dairy and cheese factories, the drying of liquid products of the slaughter-houses, etc.

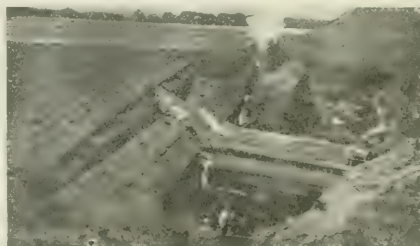
The chapter given on the various forms of apparatus used for drying purposes, both open and vacuum, is a very interesting chapter to the technologist. The book closes with a chapter on the organization of agricultural desiccating establishments and the laws of the French Republic relating to the supervision given by the state to agricultural products of this kind. Both the practical farmer and the chemical engineer will find M. Sidersky's book valuable.

H. W. WILEY.

#### SCIENTIFIC AND INDUSTRIAL SOCIETIES.

##### AMERICAN CHEMICAL SOCIETY.

The excursion of the American Chemical Society to the Pacific Coast and the meeting at San Francisco were two of the most pleasurable undertakings in the history of the Society. About



100 members and guests were aboard the Santa Fe special train when it pulled out of Chicago on the evening of July 4th.

The Chicago section entertained the travelers with a reception and buffet luncheon during the afternoon and saw them off at the station. All events took place according to the pre-arranged schedule and no mishaps occurred until the morning of Tuesday, July 12. At 6 A.M. that day, while the train was a few hours out of San Francisco, it left the track at a curve, killing the engineer and fireman instantly and mortally injuring the conductor. Most of the party were in their berths. A few were hurt, but none seriously. The cause of the acci-



dent appeared to be too high speed on a series of curves. The buffet and baggage car were demolished, the diner turned over and partly smashed, the tourist (steel) not badly damaged, the compartment thrown upward so that one end was several feet in the air. Only the last two cars remained on the track. In these two cars the party was promptly taken to King City, breakfasted, and then on to San Francisco. On account of the wreck the Santa Clara and Palo Alto trips had to be abandoned.

The remainder of the meeting was most enjoyable. On Friday and Saturday the party broke up, some going to Salt Lake, some to Seattle, where they were again entertained, and some on to the Canadian Rockies. A few made the Alaska trip. The meetings of the Division of Industrial Chemists and Chemical Engineers are reported in detail below.

#### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS OF THE AMERICAN CHEMICAL SOCIETY.

San Francisco Meeting, July 14 and 16, 1910

THURSDAY, JULY 14TH.

The session of July 14th was held at St. Francis Hotel, San Francisco, and was called to order by W. R. Whitney. The reading of the minutes was omitted. The Secretary reported for the Executive Committee as follows:

The name of the "Committee on Definition of Trade Terms" was changed to "Committee for the Definition of Industrial Terms," upon request of the Committee Chairman. Likewise the term "Committee on Advertising" was changed to "Committee on Publicity." Reports were then read from the several outstanding committees of the Division.

(1) Report of the "Committee for Definition of Industrial Terms," Clifford Richardson, Chairman, presented by George P. Adamson.

The meeting for organization was held in New York on February 14, 1910, at which all the members were present. The subject of the work of the committee was discussed at some length, and it was agreed that sub-committees be organized as follows, of which the gentlemen named were invited to become chairmen as stated:

Definition of "Bronze," Mr. J. B. F. Herreshoff, *Chairman*.

Definition of "High Grade Inorganic Chemicals," Mr. Geo. P. Adamson, *Chairman*.

Definition of "Heavy Chemicals," Mr. T. Lynton Briggs, *Chairman*.

Definition of "Pharmaceutical Products," Mr. Geo. D. Rosengarten, *Chairman*.

Definition of "Iron and Steel," Dr. A. S. Cushman, *Chairman*.

Definition of "Portland Cement," Mr. Clifford Richardson, *Chairman*.

Definition of "Petroleum Products," Mr. Clifford Richardson, *Chairman*.

Subsequently a "Committee on the Definition of Bitumen and Asphalt" was organized, consisting of the same individuals who constitute a sub-committee of the American Society for Testing Materials.

The various chairmen of the sub-committees have reported as follows in regard to the individuals that they have associated with them in their particular work.

*Sub-Committee on "High Grade Inorganic Chemicals."*—Mr. George P. Adamson, *Chairman*, Dr. L. F. Kebler, Mr. Campbell K. Walters, Mr. D. L. Murray, Mr. John T. Baker.

*Sub-Committee on "Pharmaceutical Products."*—Mr. George D. Rosengarten, *Chairman*, Dr. W. J. Schieffelin, Mr. Edward Mallinckrodt, Jr.

*Sub-Committee on "Iron and Steel."*—Dr. A. S. Cushman, *Chairman*.

Dr. Cushman will associate himself with the Committee of the American Society for Testing Materials, who are considering the subject.

*Sub-Committee on "Petroleum Products."*—Mr. Clifford Richardson, *Chairman*, Mr. T. T. Gray, Jr., Mr. P. H. Conradson.

This committee has asked for the views of various manufacturers of petroleum products, and Mr. M. Saybolt, of the Standard Oil Company, has submitted the following conclusion:

"*Naphtha*.—A generic term (light or heavy) that distills from petroleum before the lightest illuminating oil, be it *crude* or refined.

"*Gasolene*.—Both refer to refined naphthas.

Gasolene to a light refined naphtha.

"*Benzine*.—To a heavy refined naphtha.

"*Kerosene*.—A generic term for illuminating oils distilling from petroleum after heavy naphtha and before light lubricating oils."

As yet the manufacturers do not seem willing to limit the various classes by density, probably owing to the fact that the greater demand for the lighter products has compelled them to change these considerably from time to time.

*Sub-Committee on "Bitumen and Asphalt."*—Mr. Clifford Richardson, *Chairman*, Dr. Albert Sommer, Dr. A. S. Cushman, Mr. S. P. Sharples.

It has been thought best to delay the appointment of further committees until it has been determined how satisfactorily the few which have been named accomplish their work, and how the attempt to define industrial terms will be received by the producer and the consumer.

Your committee sent to the various trade journals of the country a statement of its objects as follows, which it asked them to put before their readers:

"Definition of industrial terms. At the recent annual meeting in Boston of the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, a committee was appointed by the chairman "On the Definition of Industrial Terms" to cooperate as far as possible with trade organizations in the several lines of industry in formulating definitions of their products which shall be as accurate and as fair as possible to the interests involved. The organization of such a committee has been suggested by various interests who desire a more author-



itative definition of some industrial terms, such as 'petroleum ether,' 'gasoline,' 'gasolene,' 'benzol,' 'bronze,' 'benzine,' 'steel,' 'Portland cement,' etc. It is proposed, when an interest is expressed for the definition of terms in any special field of industry, to organize a sub-committee to consider this field and define the principal terms in use in it. The committee is desirous of receiving suggestions from all who are interested in the subject as to terms which are considered the most important to be defined at the present time, owing to ambiguities which may now exist, and as to the best methods of accomplishing the work. The value of authoritative definitions as approved by the Industrial Division of the American Society will, of course, be recognized. Communications should be addressed to Clifford Richardson, 30 Church Street."

This has appeared in several of the journals, and from some of the editors, letters of appreciation of the work have been received.

With the organization of the sub-committees, the work for which the committee of the Division was appointed, has been organized, and it remains to be seen how much support it will receive. In consequence, this may be regarded merely as a progress report, and it is to be hoped that that which will be presented at the annual meeting will mark satisfactory progress.

COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS,  
(Signed) CLIFFORD RICHARDSON, *Chairman*,  
J. B. HERRESHOFF,  
GEO. P. ADAMSON.

(2) Report of "Committee on Official Specifications," Harvey J. Skinner, *Chairman*.

The committee was necessarily delayed in starting its work owing to the continued illness and subsequent death of one of its members, Dr. Rudolf de Roode. Mr. Robert Job, of the firm of Booth, Garrett & Blair, Philadelphia, Pa., was appointed to fill the vacancy.

It has been necessary to carry on a large part of the work by correspondence on account of the geographical location of the various members of the committee.

After carefully considering the problem set before them, the committee was of the opinion that the materials which should receive first consideration are those of a more strictly chemical nature, or those whose properties depend largely upon their chemical characteristics. The committee decided to carry out the ideas of the Division by the appointment of sub-committees—one for each material to be studied, the personnel of these sub-committees to consist so far as possible of three members—two representing the consumers and one the manufacturers. The following materials have been selected for our first consideration and committees appointed for each material:

Muriatic acid.	Soda ash.
Nitric and mixed acids.	Caustic soda.
Sulphuric acid.	Sulphate of soda.
Alum.	Solder.
Bleaching powder	Turpentine.

The personnel of these sub-committees is as follows:

*Muriatic Acid*.—Fritz H. Small, *Chairman*, Craton & Knight Mfg. Co., Worcester, Mass.; J. T. Baker, J. T. Baker Chemical Co., Phillipsburg, N. J.; J. O. E. Trotz, American Steel & Wire Co., Worcester, Mass.

*Nitric and Mixed Acids*.—Arthur M. Comey, *Chairman*, E. I. du Pont de Nemours Powder Co., Chester, Pa.; Henry Howard, Supt. Merrimac Chemical Co., Boston, Mass.; Oscar W. Pickering, 42 Holden St., Malden, Mass.

*Sulphuric Acid*.—Fred B. Porter, *Chairman*, Chemist Swift Fertilizer Works, Atlanta, Ga.; W. M. Kelsey, Supt. Acid Department, Mineral Point Zinc Co., Depew, Ill.; F. C. Robinson, Chemist Atlantic Refining Co., Philadelphia, Pa.

*Alum*.—William M. Booth, *Chairman*, Syracuse, N. Y.; F. A.

Olmsted; Arthur D. Little, Inc., 93 Broad St., Boston, Mass.; S. W. Wilder, Merrimac Chemical Co., 33 Broad St., Boston, Mass.

*Bleaching Powder*.—W. P. Atwood, *Chairman*, Hamilton Mfg. Co., Lowell, Mass.; Fred W. Farrell, Emerson Laboratory, Springfield, Mass.; Charles E. Acker, 97 Cedar St., New York City.

*Soda Ash*.—Henry W. Hess, *Chairman*, Libbey Glass Works, Toledo, Ohio; Martin L. Griffin, Emerson Laboratory, Springfield, Mass.; A. F. Shattuck, Solvay Process Co., Detroit, Mich.

*Caustic Soda*.—W. K. Robbins, *Chairman*, Amoskeag Mills, Manchester, N. H.; James W. Loveland, Works Manager, B. T. Babbitt, Babbitt, N. J.; J. D. Pennock, Semet-Solvay Co., Syracuse, N. Y.

*Sulphate of Soda*.—G. E. Barton, *Chairman*, Whitall-Tatum Co., Millville, N. J.; Herbert Hollick, Supt. General Chemical Co., Camden, N. J.; W. D. Livermore, Chemist Washington Mills, Lawrence, Mass.

*Solder*.—Carl F. Woods, *Chairman*, Secretary; Arthur D. Little, Inc., 83 Broad St., Boston, Mass.; W. M. Corse, Lumen Bearing Co., Buffalo, N. Y.; George O. Bassett, Western Electric Co., 463 West St., New York City.

*Turpentine*.—J. E. Teeple, *Chairman*, Hudson Terminal, 50 Church St., New York City; C. H. Hertzy, University of North Carolina, Chapel Hill, N. C.; L. F. Hawley, U. S. Forest Service, Washington, D. C.

Other sub-committees will be appointed from time to time, but it seems advisable to allow sufficient time to elapse to determine the progress made by those already appointed.

The standing committee is considering a standard form for these specifications, while the sub-committees are studying the requirements which are to be specified, and it is to be hoped that at the annual meeting in December the committee will have some finished specifications to submit to the Division.

(Signed) H. J. SKINNER, *Chairman*.

(3) "Committee on Special Compounds," Gellert Alleman, *Chairman*.

"The committee which you appointed to inquire into the prices of elements and compounds has gathered considerable information, and will have this properly tabulated and ready for presentation at the winter meeting.

"The committee earnestly requests that those who have information regarding the prices at which the rare elements may be obtained, will communicate such information for publication."

(Signed) GELLERT ALLEMAN.

(4) "Committee on Trade Customs,"

The Secretary read a letter from Henry Howard, Chairman of the committee indicating that there was apparently no interest among the manufacturing chemists in the proposed work of this committee—whereupon the motion was made from the floor that the committee be discharged. The motion was carried.

(5) "Committee on Research Problems," George C. Stone, *Chairman*.

"The Committee on Research Methods of the Division of Industrial and Engineering Chemistry" have to report that, after meetings and correspondence, they published a circular in the May number of THIS JOURNAL, requesting suggestions and assistance from the members. In this circular they outlined the work they believed it practicable for them to undertake and in almost all lines the co-operation of the members of the Society is essential, and those who are willing to assist were asked to communicate with the committee. The replies have been so few as to be very discouraging and show a complete lack of interest in the work of the committee by the members.

The committee will meet as soon as possible and endeavor to discover other possible lines of work that will be of use to the

Society and that can be carried on without assistance from the membership at large.

(Signed) GEORGE C. STONE, *Chairman*.

(6) "Committee on Standard Methods of Technical Analysis."

The chairman made a statement referring to the handicap under which this committee had labored during the past several months, owing to the misunderstanding as to the relation between its Committee and the Parent Society Committee on the Standard Methods of Analysis. By recent action of the Council all questions as to the relations between the General and Divisional Committees have been regulated so that this Committee is now free to proceed with the very important work for which it was designed.

No definite reports were received from the Committee on Descriptive Bibliographies or from Committee on Advertising.

Papers comprising symposium on smelter smoke were then presented as follows:

(1) Charles Baskerville, "The Smoke Problem and the Community." In the absence of the author this paper was read by the Secretary. It dealt mainly with legal questions involved, and summarized the most important decisions, both American and foreign.

(2) W. C. Ebaugh, "The Neutralization and Filtration of Smelter Smoke."

This paper was supplementary to previous articles that have been published in the *Journal of the American Chemical Society* and THIS JOURNAL. The removal of solids from smelter fumes has greatly reduced the damage to surrounding vegetation and apparently promises a fair solution of the problem.

(3) F. G. Cottrell, "The Electrical Precipitation of Suspended Matter."

By the use of numerous lantern slides the author indicated the development, from the crude laboratory stage to the successful commercial installation, of his process for the precipitation of either solid or liquid suspensions from gases by the use of high potential electrical discharge. This interesting description was supplemented on the following day by demonstrations of the laboratory apparatus at University of California, and of the commercial installation at the plant of the Selby Smelting and Lead Company. This same process in a modified form is utilized in separating oil-water emulsions. This has proved commercially successful in the recovery of large quantities of California crude oil previously of little value because of the great permanency of the emulsions.

The discussion following the symposium was necessarily restricted as California hospitality not only left no time for extra sessions but intruded somewhat upon the time specified in the program. It is thus necessary to record that the meeting scheduled for July 15th at the University of California was by common consent omitted as otherwise there would have been no opportunity for visitors to inspect the numberless attractions that were to be discovered there.

SATURDAY, JULY 16TH.

At the meeting held at St. Francis Hotel, San Francisco, W. C. Ebaugh acted as temporary chairman.

The following papers were presented by the authors:

(1) W. C. Ebaugh, "The Composition of Solids Precipitated from the Atmosphere during a 'Salt Storm,'"

(2) Elwood Haynes, "Alloys of Nickel and Cobalt with the Metals of the Chromium Group."

(3) W. C. Blasdale, "Factors Affecting the Electrolytic Method for the Determination of Copper in Ores."

(4) George Kemmerer, "The Electrolytic Determination of Zinc in Ores."

There was also transferred from the Division of Physical and Inorganic Chemistry the two following papers:

(5) Charles H. Herty and E. N. Tillett, "The Unsaturated Character of the Resin of *Pinus Sabiniana*."

(6) Charles H. Herty, W. A. Houck and T. P. Nash, "A Study of the Resin of *Pinus Heterophylla*."

The following papers were read by the Secretary in the absence of the authors:

(7) A. F. Greaves-Walker, "Scum or Efflorescence on Brick."

(8) Kenneth Williams, "The Influence of Varying Quantities of Litharge in an Assay Charge."

(9) Leon Labonde, "The Scientific Use of Crude Petroleum as a Source of Power."

The following papers were read by title only:

(10) J. T. Baker, "Problems in Industrial Chemistry."

(11) Charles P. Fox, "The Cuban Hedge Cactus: a Proposed Source of Crude Rubber."

(12) Charles P. Fox, "*Ficus Elastica* in Florida."

(13) W. D. Richardson, "Rust as an Accelerator in the Corrosion of Iron and Steel."

(14) L. W. Bahney, "Rapid Estimation of Available Calcium Oxide in Lime Used in Cyanide Work."

Previous to adjournment the Division passed a resolution of thanks to the California Section for their hearty entertainment and many courtesies and to the several industrial plants which by opening their works for inspection contributed a great deal to the technical interest of the meeting.

F. E. GALLAGHER, *Secretary*.

ABSTRACTS OF PAPERS READ BEFORE THE SEMI-ANNUAL MEETING OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, NIAGARA FALLS, CAN.,  
JUNE 22ND TO 24TH, 1910.

PROBLEMS IN CHEMICAL INDUSTRY.

By JOHN T. BAKER, Phillipsburg, N. J.

The number and complexity of the factors involved in chemical operations are so great that many operations are still carried on under the rule of thumb guidance and have not been reduced to a science. On the other hand, the trained scientific man is very prone to believe that the matter with which he deals will follow the laws which he has learned, and for this reason he often overlooks valuable facts which the untrained observer sees. The untrained observer ignores laws and systems, tries any suggestion that comes along, and therefore loses much valuable time and labor. The investigator who is successful follows a mean between these paths. A number of practical illustrations of these principles were given.

COMMERCIAL CALCIUM HYDRATE, ITS MANUFACTURE AND USES.

By LUCIUS E. ALLEN,<sup>1</sup> of New York.

This paper gives an outline of the method of manufacture of this product and calls attention to the many cases in which it can be used to better advantage than the unslaked lime. It is well adapted for water-proofing Portland cement. Its keeping qualities are excellent.

A NEW PRODUCT FOR USE IN THE ARTS.

By DR. F. G. WIECHMANN.

The base of this new material is vegetable-albumin, under which generic term, vegetable ivory, the vegetable caseins, glutens, hemi-celluloses, reserve-celluloses, horny-albumins, etc., are included.

The vegetable-albumin, from whatever source derived, is treated with one or more substances which convert it into a new substance, a plastic, eminently well adapted for use in the arts and industries. To this new plastic the name "Protal" has been given.

<sup>1</sup> Read by N. L. Turner.

Any and all materials commonly used in the rubber industry may be incorporated with protal. About one hundred different protal compounds have been produced and, of course, the properties of these compounds vary with the ingredients employed.

Protal can be molded, pressed, or otherwise formed into any desired shape. It is odorless, resilient, and can be cut, sawed, filed, polished, tapped and countersunk, like hard rubber. It can be colored by dyes, and all pigments can be incorporated with it. It is non-explosive and is very resistant to the influence of heat and electricity.

Among the great number of protal compounds which have been made, there are some which contain rubber, rubber substitutes, shellac, rosins, asbestos, etc. Some of these products remain plastic and moldable for a long time and possess the remarkable quality of hardening on immersion in water.

Compounds of protal with rubber, rubber fluxes and some of the so-called rubber substitutes, exhibit a wide range in their properties. They can be made hard, semi-hard and soft, which of these qualities they are to exhibit being determined by the choice of loading materials and by the conditions of heat and pressure governing their production.

Among the most important compounds of protal, is Protal-Bakelite—bakelite being that most interesting and valuable product, the discovery of which was announced last year by Dr. L. H. Baekeland, of Yonkers, N. Y., and which is, as is well known, a condensation product of phenol and formaldehyde.

Protal-Bakelite possesses many valuable qualities. It exhibits great resistance to nearly all chemical solvents. It is an excellent electric insulator, is capable of taking a high degree of polish, can be produced in almost every color, and is well adapted to the many purposes and uses for which hard rubber and hard rubber compounds are, at present, almost exclusively employed.

It possesses the great advantage over hard rubber of not being subject to oxidation, of not softening on the application of heat and of not being attacked by oils and bodies of a similar nature.

Any and all materials, organic as well as inorganic, may be incorporated with protal-bakelite, thus giving rise to a great number of compounds which possess very different qualities and properties and which are adapted to a great variety of uses.

Protal-Bakelite compounds have, as before said, great dielectric strength, ranging from about ten thousand volts to about twenty-six thousand volts per millimeter.

It would be practically impossible to specify all of the uses to which this new plastic may be put. It need only be borne in mind that this is a plastic which can be fashioned into any shape, which can be molded and pressed, which is capable of taking a high polish, which is not affected by water—cold or boiling—which is resistant to practically all chemical solvents, which can be tooled and machined with ease and which is produced in both flexible and rigid form.

In cost, this material compares very favorably with rubber and every day witnesses its introduction into new fields of industry.

The manufacture of protal and protal-bakelite is in the hands of a New York concern, Protal Company, the works being located at Bridgeport, Conn., and at Yonkers, N. Y.

#### THE STUDY OF MATERIALS AS A SUBJECT IN A COURSE OF CHEMICAL ENGINEERING.

By CHAS. F. MCKENNA.

Dr. McKenna calls attention to the fundamental importance of a thorough knowledge of all the properties, both physical and chemical, of the materials available for human use. The

extraordinary number of substances used in the arts is surprising. A careful list of those used by one company comprised no less than 850 definite and distinct classes or grades of materials.

The chemical engineer must study the properties of these materials because it is he who must transform the raw properties of nature into products possessing properties which make them of use to mankind.

A careful classification of the tests, both physical and chemical, to be applied is given. No material, even the most common, has as yet been fully investigated and all of its properties discovered. The adoption of the so-called standard or uniform methods of analysis are apt to discourage rather than encourage the investigation of the properties of materials.

#### CHANGES IN INDUSTRIAL CHEMISTRY CAUSED BY ELECTRICITY.

By EDWARD R. TAYLOR, Penn Yan, N. Y.

This paper calls attention to the advantages to be derived from the use of electricity with the object of stimulating the development of water powers.

The great advances already made in a number of industries especially metallurgical, and in the production of alkali and bleach, is reviewed. It is shown that these industries could be carried on commercially only after water power is developed. The electric separations and determinations of metals now carried on only in the quantitative laboratory indicate what may be accomplished on an industrial scale in the near future. The manufacture of chlorine and ozone in small units indicate how many small industries can install their own plant for using chlorine and ozone for bleaching, cleaning, disinfecting, etc.

Among the new uses for electricity was mentioned the very marked increase in the quality and quantity of yield of various agricultural products when electricity was allowed to leak into the soil.

Twenty-four electric furnaces for the smelting and refining of iron and steel are at present in operation.

The large amount of water power which is allowed to go to waste at present was deplored.

#### THE DEVELOPMENT OF CHEMISTRY INDUSTRY IN CANADA.

By JUDSON A. DECREW, Montreal, Can.

This paper treats of the various industries of a chemical nature that are established in Canada, and show where statistics or dates are available, the rapid development that has taken place in this field within the last 5 or 10 years.

An attempt is made to give the location of the various works and, where possible, the approximate capacity at the present time.

The industries mentioned, and concerning each of which some facts are given, are as follows:

Sulphuric Acid and Alkali. Coal Tar and Ammonia. Explosives. Fine Chemicals. Wool Distillation Products. Petroleum, Salt, Milk, Sugar, Starch, Rubber, Glue. Paints, Fertilizers, Glass, Beverages, Soap and Glycerine. Calcium Carbide and Electrochemical Products. Wood Cellulose Products. Portland Cements.

Reference is also made to several new projects that are still in the stage of development, but which may soon be classed among the established industries.

#### NOTE ON THE CORROSION OF IRON AND STEEL AND ITS PREVENTION.

By GUSTAVE W. THOMPSON, Brooklyn, N. Y.

This paper gives a most excellent summary of the facts which have been discovered with reference to the cause and prevention of the corrosion of iron and steel. The author leaves it to the reader to interpret these facts in the terms of any theory



with which he may be familiar. The general conditions conducive to the formation of rust are first given. The opinion is given that facts do not warrant the conclusion that the tendency of iron to corrode is dependent on the composition of the metal and that the use of a purer and more expensive metal as against a more impure and cheaper metal is not justified by the facts.

Practical suggestions with reference to the prevention of corrosion of iron and steel are given, among which the following may be mentioned: The action of acids, moisture and oxygen. Cement prevents corrosion because it is alkaline. Protective coatings exclude moisture and oxygen. The cleaning of iron and steel before painting is of great importance. Specific rules for the cleaning of steel and iron are given as well as the value of the various methods in common use.

The principles which should guide in the selection or designing of the paint are given. Poor workmanship in the application of paint was given as responsible for most of the failures in the protection of iron and steel with paint. Linseed oil was condemned as a prime coat for iron and steel.

Nineteen different paints applied to the Havre de Grace Bridge of the Penn. R. R. all proved equally effective because they were properly applied. Oxygen cannot be excluded from iron by means of any protective coating. In the absence of moisture, oxygen does not produce corrosion.

#### THE MANUFACTURE AND INDUSTRIAL APPLICATIONS OF OZONE.

By DR. OSCAR LINDER, Western Electric Co., Chicago, Ill.

The properties and methods of formation of ozone were given. The amount present in pure air was given as about 1 part in 1,000,000. The commercial methods of manufacture of ozone are almost exclusively electrical, although ozone is formed by the ultraviolet light and heat. The successful operation of the electric ozonizers depends upon the rise of a high voltage (10,000-40,000 volts) and dry air maintaining a low temperature. Concentrations of ozone as high as 50 grams of ozone per cubic meter of air corresponding to 2 per cent. by volume have been obtained. Yields of 105 to 250 grams of ozone per kilowatt hour have been obtained.

Ozone has been used industrially for a great many purposes. The purification of the air of theatres, schools, restaurants, and public halls is quite common in Europe. Ozonizers made especially for ventilating purposes are now on the market and are made either of portable or stationary type. Large installations for water purification are in successful operation.

Ozone is well adapted for sterilizing and disinfecting purposes. It is being tested in the Quarantine Station in New York and at the Pittsburg Homeopathic Hospital. It is believed that ozone will ultimately supplant formaldehyde in disinfecting rooms and buildings. It has also been successful for the preservation of milk, cream, butter, eggs, fruits, meat, etc.

Ozone is also an excellent bleaching agent.

#### PLANT DESIGN.

By W. M. GROSVENOR, New York.

In this paper a number of very practical suggestions are made with reference to plant design. Illustrations are given showing the advantage of handling materials by the gravity system. The installation of complicated systems of conveyors is declared to be generally poor policy on account of the usual high cost of maintenance.

The importance of careful management of materials in construction is emphasized. A loss of \$10,000 worth of material was reported in one case on account of poor storage facilities during construction.

#### NITRIC ACID.

By SCHUYLER FRAZIER, Chicago, Ill.

This paper gives a few notes with reference to the manufacture of nitric acid. The various important advances which have been made in recent years are reviewed, and the advantages secured by each improvement is noted. Tables giving the yield and purity of acid obtained, as well as rate of distillation, are appended.

#### UNDERGROUND WATERS FOR MANUFACTURING PURPOSES.

By W. M. BOOTH, Syracuse, N. Y.

The paper gives reasons why underground water is or should be sought, also what preliminary steps should be taken in locating the wells, well surveys and records. The cost of drilling is discussed and the employment of a drilling company is considered. The importance of the chemist as an aid in well drilling and the quality of water to be expected from different strata is discussed. Examples are given showing methods and cost of pumping. The quality of water found in average wells at different depths and cost of treating well waters for manufacturing purposes is fully discussed.

#### COAL: ITS DETERIORATION IN STORAGE.

By A. BEMENT, Chicago, Ill.

Results of experiments given in this paper are the termination of a long period of study with the two coal seams of Illinois, which from the standpoint of production are the most important ones. The experiments show changes in heating power, in quality of the fuel, and disposition to slack down to smaller size during storage.

### RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**960,441. Production of Fine-metal Tungsten.** ELIHU THOMSON, of Swampscott, Massachusetts. June 7, 1910.

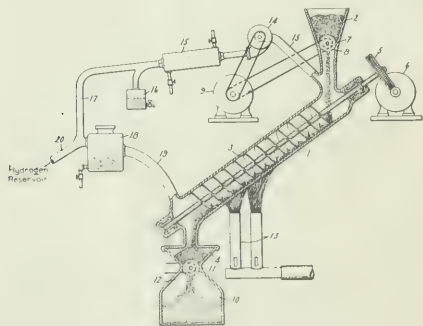
This invention relates to the reduction of metals by a gaseous reducing medium.

It is desirable for some purposes to obtain metals in a finely divided state, with the exclusion of all impurities. A very pure, finely divided metal can be best obtained by carefully purifying some reducible compound of the metal, as the oxid, and then effecting a reduction of the finely divided oxid with a pure reducing gas, as hydrogen. As finely divided metals are easily oxidized when heated, great care must be used to guard against the heated reduced metal coming in contact with air, or the watery vapor which results as a by-product in the reaction.

According to this invention there is employed a furnace which will accomplish a continuous reduction of metallic compounds, as tungsten oxid, at any desired rate, using for this purpose a reducing gas, such as hydrogen. As only a small part of the hydrogen is used up in the reaction when hydrogen gas is passed over a metallic oxid, I provide for the removal of the watery vapor, and return the hydrogen to the furnace to be again used in the reducing process.

The reduced tungsten compound, as tungstic oxid,  $WO_3$ , is conveyed into the tubular-inclined reducing chamber 1 from the hopper 2. The reducing chamber is provided with a rotatable Archimedeian screw, 3, which serves to move the oxid along the reducing chamber at any desired rate. The reduced metal

falls into the receiving hopper 4. The Archimedean screw is rotated at any desired rate, and is connected by means of the gear 5 to any suitable source of power, such as the motor 6. The hydrogen enters at the opposite end of the reducing chamber and passes through the same. The streams of oxid and hydrogen, therefore, move in opposite directions. The reducible oxid is conveyed into the reducing chamber 1 from the hopper 2 by means of the rotatable member 7, which is provided with a slotted portion, 8. The rotatable member 7 is connected to any suitable source of power, as the motor 9, and in its revolution the slotted portion 8, in passing through the hopper containing the oxid, "picks up" a portion of oxid and transfers

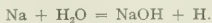


it to the reducing chamber. By this arrangement the oxid is fed uniformly into the furnace and air is kept out of the reduction chamber. The reduced metal is conveyed out of the hopper 4 into a receiving vessel, 10, in a similar manner by means of the rotating member 11, which is likewise provided with a slotted portion, 12.

The reducing chamber is heated through a portion of its length by any suitable means, such as the gas burners 13. The temperature of this hot zone should be somewhere between 600–800° C. As the dry hydrogen gas meets the tungstic oxid in the hot zone, reduction takes place according to the following reaction:



As before stated, the stream of hydrogen and the tungstic oxid move in opposite directions, therefore the watery vapor resulting from the reaction is carried by the hydrogen away from the reduced metal, and re-oxidation is, therefore, avoided. The linear speed of this moving stream of hydrogen must be great enough to carry away the moisture at a rate which will exceed the rate of diffusion of the watery vapor in the opposite direction. The hydrogen, laden with watery vapor, is drawn from the reducing chamber by means of a pump, 14, through a tube, 15. The pump may be connected to any suitable source of power. As shown on the drawing, it is connected to the motor 9. The hydrogen is conveyed by the pump through a water-cooled condenser, 15, where a greater part of the watery vapor is condensed. The condensed moisture trickles down into a receiving vessel, 16. The unused hydrogen still containing a certain amount of uncondensed moisture is carried by means of the tube 17 to a vessel, 18, where it comes in contact with metallic alkali, such as sodium. The following reaction takes place:



As will be seen, the hydrogen is regenerated with the formation of sodium hydroxid. The unused hydrogen, together with this regenerated hydrogen, is carried back to the reducing chamber through a tube, 19, and is used again for the purpose of re-

duction. The vessel 18, instead of containing a metallic alkali for the purpose of regenerating hydrogen from the moisture, may contain a moisture-absorbing agent, such as sulphuric acid or calcium chlorid, and the moisture may thus be absorbed, the unused hydrogen, as before, being returned to the reducing chamber. In either case any losses of hydrogen are made good by the introduction of hydrogen from a hydrogen reservoir through a tube, 20.

960,542. Means for Recovering By-Products. PULASKI M. HAMLIN, of Pittston, Pennsylvania. June 7, 1910.

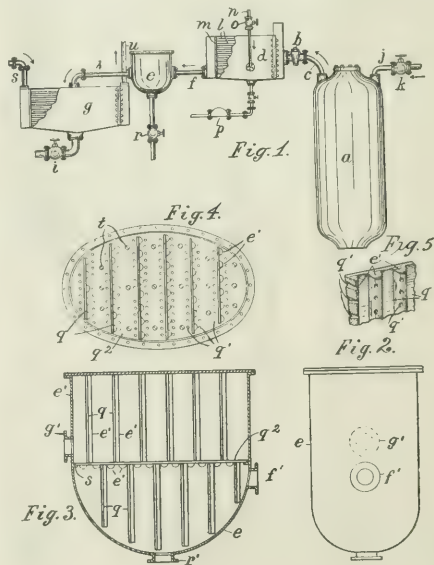
This invention relates to a means of recovering volatile by-products from the treatment of wood-fiber or other crude materials in a cooker, digester, or roaster in which the crude material is heated to change its constitution, and the by-products are incidentally vaporized.

When it is desired to maintain any pressure above the atmosphere during the treatment of the crude material, such pressure can be obtained and the by-products secured by discharging the vaporized by-products from the receptacle only as fast as they are generated, which is effected by any valve suitable for regulating and limiting the discharge flow.

The invention is partly adapted for the recovery of turpentine oils, resin, and wood alcohol from wood during the manufacture of pulp without interfering with the pulp-making, or increasing its cost. In such manufacture of wood-pulp, a charge of wood-chips is placed in a tightly closed digester and is heated by injecting steam into the digester at a temperature above the boiling point of the by-products, which are thus necessarily vaporized.

In digesting coniferous woods to produce pulp, ingredients of greatly different character and density, as wood alcohol and resin, are discharged as by-products, and the object of the present invention is to first separate the heavier ingredients from the vapor in order that they may not clog the water-cooled condenser which is required to liquify the more volatile elements.

Resin and heavy oils if condensed upon a chilled surface adhere strongly thereto and are liable to accumulate and clog



up the vessel in which they are condensed so that its use cannot be continued without frequently opening it to remove these gummy substances. The patentee has discovered that an air-cooled trap suffices to separate such heavier elements from the vapor, while it does not chill them sufficiently to prevent their spontaneous flow from the trap. He forms the trap with perforated baffle-plates which afford an extended surface for the deposit of these gummy elements and the conveying of their heat to the atmosphere, the plates producing a deposit of these elements without preventing their flow and discharge from the trap at the temperature of the air which is always much below that of steam under pressure. That portion of the vapor which is uncondensed in the air-cooled trap is then treated in a surface condenser where tubes can safely be used as a cooling agent, because the elements condensed from the remaining vapor are of a fluid character and not liable to clog the passages between the pipes by adhesion thereto. The apparatus does not separate all the by-products from one another, but divides them into two very different classes which are adapted for very different subsequent treatment to dissociate them, as may be desired.

The discharge of vaporized by-products from the digesters during the cooking operation permits steam, watery vapor and crude materials to pass off with the vapor, and it is therefore found desirable to reheat this vapor at a temperature higher than that in the digesters so as to fully volatilize all the watery vapor and any of the crude materials that have not been vaporized.

The illustration shows the patentee's apparatus.

**961,121. Process for Cleaning Iron Ores.** EDWARD F. GOLTRA, of St. Louis, Missouri. June 14, 1910.

This invention relates to a process for cleaning iron ores and for preparing the same for the subsequent operations.

Some iron ores, as brown hematite, contain a large percentage of clay and sometimes silica as a gangue, and this gangue must be separated from the ore before it can be used in a blast furnace.

The apparatus illustrated consists of a runway upon which the ore is thrown. The ore on the runway is subjected to a strong blast so as to dry the gangue and render the earthy, the silicious and any other gangue easily separable from the ore. The ore is tumbled to shake loose the gangue from the ore, and the gangue is removed by the blast.

The runway is preferably in the form of a long inclined tube or drum, which is rotated about its longitudinal axis, and a hopper is located at one end of the drum for discharging the ore in the same. The ore in its passage downwardly is heated to dry out the ore and render the gangue brittle and easily separable from the ore, and the rotation of the drum will tumble and rattle

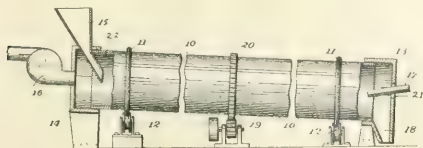
the fresh ore admitted from the hopper this hot blast is cooled down enough so that its temperature is sufficiently low to prevent the hard baking and burning of the gangue.

The ore as mined is crushed so as to reduce it to workable form. It is not necessary to pulverize it, but it is sufficient if it can pass through a two or two and one-half inch mesh. This crushed ore is placed in the hopper 15 and is discharged into the drum 10. The burner 17 furnishes the necessary heat and the temperature will be the greatest at the lower end of the drum, but at the upper end this temperature will be considerably reduced, so that the fresh wet ore will not be heated to a sufficient degree so as to hard bake the gangue. As the ore moves downwardly it will be tumbled and thrown around so as to knock loose all of the gangue which clings to it, this gangue becoming more and more heated and more and more loose, dried and pulverized as it proceeds toward the lower end of the drum. The ore is cleaned and washed of its gangue by the blast passing through the drum, the gangue being drawn off by the strong blast which is created by the suction fan 16. The drum is made long enough and the speed of rotation is governed so that at the time when the ore reaches the discharge 18 practically all of the gangue has been dried out and rendered separable, shaken off of the ore and drawn off by the blast. Since the temperature will gradually increase from the upper to the lower end of the drum, the ore is gradually dried and thus the gangue is rendered very brittle, and due to this gradual increase, the gangue on the ore as it is admitted will not be subjected to the high temperature as would be the case if the burner 17 were placed at the upper end of the drum.

It will be noted that the blast is passed through and above the ore while it is agitated. The rotation of the drum will cause the ore to rise with the sides of the drum and fall through the blast passing through the drum. In this way the strong blast sweeps the pulverized gangue clinging to and surrounding the ore with it, allowing the cleaned ore to pass down the drum to the discharge 18.

**961,350. Process of Making Nitric Acid.** FRIEDRICH HAUSER, of Kaiserslautern, Germany. June 14, 1910.

It is known that at high temperatures nitrogen and oxygen combined directly with each other so as to form oxid of nitrogen which at ordinary temperature further combines with oxygen so as to form dioxid of nitrogen, which will produce nitric acid when dissolved in hot water. This method of producing nitric acid has been carried out on a commercial scale in North America, especially at the Niagara Falls where the oxidation of the nitrogen has been effected by means of the electric arc. It is, however, expensive to produce in this manner the high temperatures required for manufacturing nitric acid and it has been found that in order to obviate said inconveniences the oxidation of nitrogen can be effected in a more economical way by means of explosive combustion, that is to say, by heating or burning a mixture of nitrogen gas and oxygen gas for instance in an explosive engine, together with a suitable fuel, as coal-gas, benzene-vapor or the like, and preferably after the said gas mixture has been compressed, prior to ignition, adiabatically, as far as possible as the gain in oxid of nitrogen very quickly increases in proportion to the rise of temperature. The formation of oxid of nitrogen being a reversible reaction it is necessary, in order to avoid any decomposition of the oxids of nitrogen formed, to suddenly chill the gas mixture at the moment of maximum temperature. Evidently the gas mixture must be cooled down to a degree where the reaction speed is so low that a decomposition of the oxid of nitrogen practically cannot take place, that is to say, to 1600° C. or lower. But as the gas mixture still exerts a high pressure at this temperature, it is profitable to allow the gas mixture to expand, after having been cooled, in a well-known manner.



the ore as it dries and cause the gangue to be shaken loose from the ore and pulverized by the tumbling action. The strong blasts sweeps, cleans and washes the gangue from the ore and this gangue is withdrawn from the drum by the blast while the cleaned ore passes along the drum to the discharge end.

The ore as mined must be dried slowly especially if it contains much clay as a gangue since a rapid heating would cause this clay to be baked hard and burned to a brick and thus it would be impossible or exceedingly difficult to thereafter loosen it from the ore. For this purpose the hot blast enters the drum at the lower end, that is at the discharge end, and when it strikes



The gain in oxid of nitrogen depends on both the explosion temperature and the proportion of nitrogen and free oxygen in the gases resulting from the explosion, that is, exhaust gases. The gain, therefore, can be increased by adding oxygen to the air used for the explosive mixture.

The most favorable proportion of oxygen and free nitrogen producing the greatest amount of nitric acid exists, if the mixture after the explosion contains the same amount of oxygen and nitrogen. This result may be obtained by adding artificial oxygen to the atmospheric air. The simplest way is, however, to use ordinary atmospheric air, in which case 100 parts of the

FIG. 1.

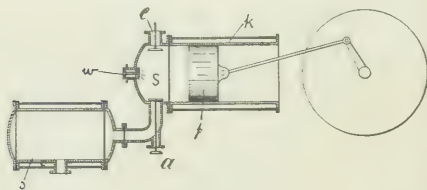
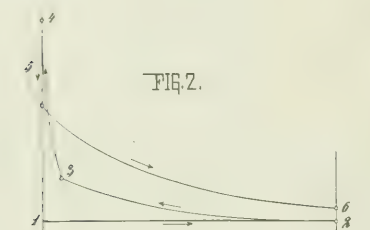


FIG. 2.



initial fresh gas mixture contain about 68 parts nitrogen, 18 parts oxygen, and 14 parts hydrocarbon vapors in the form of lighting gas. The composition of the mixture varies with the quality of the lighting gas. If the quality is good, less gas is added, and *vice versa*. The mixture having the proportions above stated is a gas having a heating value of 5,000 calories.

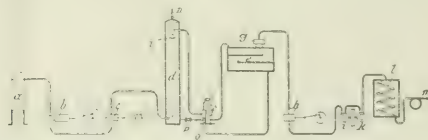
The temperature which is indicated by the point 4 in Fig. 2 should be as high as possible, because the production of nitric acid increases very much with the increasing temperature. The temperature should be preferably no less than 1900 to 2,000° C. Such temperatures can be easily obtained by a sufficiently high compression of the combustible mixture prior to its ignition and by the use of gases of great heating quality, as for instance lighting gas mixed with air.

960,788. Process for Manufacturing Carbonic Acid. ERNST AUGUST BEHRENS, of Bremen, Germany. June 7, 1910.

This process is carried out in the apparatus shown in the accompanying illustration. The gas is led from the generator *a* to the power cylinder *b* of an explosive gas engine, where it is exploded in the presence of sufficient air to convert the CO in the gas to CO<sub>2</sub>. It has been found in practice that such employment of an explosive engine furnishes almost the entire power necessary in the subsequent portions of the operation, and that the cylinder-cooling water of the explosive engine can be employed for maintaining the saline solution at the required temperature. The exhaust gases from the explosive cylinder *b* are forced by a compressor, *c*, under suitable pressure into the lower portion of a reservoir, *d*. The compressor *c* may be belted to the explosive engine, or driven in any other desired manner. The reservoir *d* is partially filled with a solution of potassium

carbonate, which is maintained at about 100° C., and the exhaust gases are forced therein by the compressor *c* at a pressure sufficient above that of the atmosphere to cause a chemical union of the CO<sub>2</sub> with the potassium-carbonate at such temperature, the upper portion of the reservoir *d* being provided with a relief valve, *n*, to permit escape of the nitrogen of the exhaust gases which accumulates in the upper portion of said reservoir. A pipe, *o*, leading from the lower portion of the reservoir *d*, conducts the solution to a tank, *e*, where it flows over baffle-plates, and, owing to the reduction of pressure, gives up the CO<sub>2</sub> in a gaseous form, a valve, *p*, being provided in the pipe *o* for regulating the rate of flow therethrough. A pump, *f*, is employed for withdrawing the solution from the tank *e* and returning it under pressure through a spray nozzle, *g*, to the upper portion of the reservoir *d*, thus establishing a continuous circulation of the solution between the reservoir *d* and the tank *e*. An aspirator and compressor, *h*, is employed for drawing the CO<sub>2</sub> from the tank *e* and forcing it under suitable pressure through the nipple *m* to retorts or other receptacles, a series of purifiers and coolers, *i*, *k* and *l*, being interposed between the compressor *h* and said nipple.

This method of absorption and setting free of the carbonic acid by pressure and relief of pressure without changing the temperature allows of a considerable saving being realized in the manufacture; it must still be added that according to the physical conditions whereupon the present process is based,



the absorption speed is considerably higher than in the known process, and owing to this fact it is possible to work with considerably less lye. It follows therefrom that the dimensions of the installation are considerably reduced in comparison with the known installations.

It has been proposed to produce carbonic acid through the influence of a partial vacuum with or without a saline solution. Experiments show that at low temperatures the separation of carbonic acid from a solution of bicarbonate of potassium, even under a high vacuum, is too slow to be of any industrial value. If the separation of the carbonic acid is produced by heating the saline solution, the latter must be cooled down before it can be again used for absorbing the carbonic acid.

961,945. Method of Manufacture of Bicarbonate of Soda. ROBERT HUGH FORSYTHE FINLAY, of Belfast, Ireland. June 21, 1910.

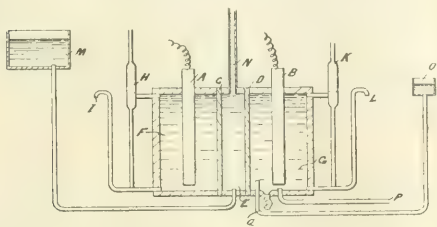
This invention relates to improvements in the method of manufacture of bicarbonate of soda, and it has for its object certain improvements in the ordinary or so-called Solvay ammonia-soda process, whereby the inventor is enabled to dispense with the necessity for distilling the liquid from which the bicarbonate of soda has been precipitated (hereinafter called the mother liquor); avoid the use of lime, and the loss of ammonia and undecomposed salt contained in the discharge from the stills after distillation—the disposal of which discharge constitutes rather a troublesome feature of the ammonia-soda process as now carried out.

The present invention, moreover, presents the advantage that the user is enabled to recover the chlorin of the salt acted upon, in the form of chlorin gas, instead of as heretofore permitting it to pass away with the discharge above mentioned in the comparatively worthless form of calcium chloride.

In carrying the invention into effect the earlier steps of the

well-known ammonia soda process is followed up to the point at which the mother liquor has to be dealt with; that is to say, the user treats the brine with ammonia and carbonic anhydrid so as to obtain a precipitate of bicarbonate of soda, ammonium chlorid being left in solution as well as some undecomposed sodium chlorid and some ammonia and carbonic anhydrid, chiefly in the form of bicarbonate of ammonia.

The precipitated bicarbonate of soda being removed and treated in the usual manner the mother liquor is passed directly, or after treatment with carbonic anhydrid, into the cathode chamber of an electrolytic cell, or battery of cells, brine being



supplied at the same time into the other chamber or chambers. The ammonium chlorid in the mother liquor is here electrolyzed, and ammonia is set free at the cathode and combines with carbonic anhydrid, if present, chlorin being also set free at the anode.

After electrolysis the liquids and gases are removed from the cathode chambers. The hydrogen formed at the same time as the ammonia is readily eliminated, being insoluble. Water also may be eliminated from the liquid by evaporation at this stage. The liquid which now contains some common salt and the ammonium chlorid which has not been decomposed by electrolysis may be used instead of brine in the first reaction of the process in which meeting with the ammonia liberated by electrolysis and carbonic anhydrid, bicarbonate of soda is again precipitated and the mother liquor again treated as described.

If salt be added to the mother liquor before, and carbonic anhydrid be injected during electrolysis, bicarbonate of soda may be formed in the cathode chamber of the cell. In this case the chamber should be made larger than would otherwise be necessary and be furnished with suitable means for removing the precipitate.

The accompanying illustration shows the apparatus in which the process is carried out.

## INDUSTRIAL AND TRADE NOTES.

(Continued from July No., p. 316.)

**Potassium Cyanid·Manufacture (Continued).**—The ceilings are 23 feet high to the cornice. In building construction the use of wood has been avoided wherever possible, and owing to the poisonous nature of the product every precaution has been taken to prevent the escape of gas into the buildings.

From the centrifugal machinery up to where the cakes of potassium cyanid are pressed and packed workmen are obliged to wear respirators and specially made gloves. On arrival at the factory workmen must change their clothing, lockers being arranged, and before leaving the works they must bathe, shower and plunge baths being provided. There is also a dining-room in an adjoining building. It is necessary to run night and day; 130 men work on each shift; no boys or women are employed. Many workmen walk three to four miles from surrounding villages. They work 11 hours, quitting at 6 A.M. or 6 P.M., according to shifts, and have one hour for meals. The common

laborers receive 41 cents and the skilled workmen 91 cents to \$1.02 per day. The trust controlling the manufacture of potassium cyanid from molasses pays \$1.52 to \$1.62 for each 220 pounds of raw material. Before the discovery of this new process the molasses was considered worthless, while there are now several more by-products of commercial value after producing the potassium cyanid.

**Production of Steel.**—The American Iron and Steel Association has just compiled its statistics for the production of open-hearth steel ingots and open-hearth castings in 1909. They show that the total was 14,493,936 gross tons, against 7,836,729 tons in 1908, an increase of 6,657,207 tons, or 85 per cent. The production in 1909 was much the largest in the history of the industry and exceeded that of 1907, the next largest year, by 2,944,200 tons, or 25.4 per cent. In 1908 the production of open-hearth steel for the first time exceeded that of Bessemer steel, the totals in that year being 7,836,729 tons and 6,116,755 tons, respectively. For 1909 the figures were 14,493,936 tons and 9,330,783 tons, respectively. The rapid increase in the production of basic open-hearth steel accounts for the record-breaking figures in 1909. The total production of basic open-hearth ingots and castings was 13,417,472 tons, while that of acid open-hearth ingots and castings was 1,076,464 tons. This last figure has been exceeded in five preceding years—namely, 1907, 1906, 1905, 1903 and 1902.

The production of open-hearth steel castings in 1909 was 601,040 tons, of which 306,005 tons were basic and 295,035 tons acid steel.

The production of crucible steel in 1909 amounted to 107,355 tons, against 63,631 tons in 1908, an increase of 43,724 tons, or 68.7 per cent. Of the total for 1909, 94,672 tons were ingots and 12,683 tons castings. The high point in crucible steel production was reached in 1907 at 131,234 tons; in 1906 the total was 127,513 tons. Last year's total was over 5,000 tons less than that of a year as far back as 1902.

The production of steel in 1909 by various minor processes, including the electric process, amounted to 22,947 tons, against 6,132 tons in 1908. Of the total last year, 14,242 tons were ingots and 87,005 tons castings.

The production of all kinds of steel ingots and castings in 1909 amounted to 23,955,021 tons, against 14,023,247 tons in 1908, an increase of 9,931,774 tons, 70.8 per cent. The production of the various kinds of steel in the past three years is as follows in gross tons:

	Bessemer.	Open-hearth	Crucible and all other	Total ingots and castings
1909 . . . .	9,330,783	14,493,936	130,302	23,955,021
1908 . . . .	6,116,755	7,836,729	69,763	14,023,247
1907 . . . .	11,667,549	11,549,756	145,509	23,362,814

Included in the 23,955,021 tons of steel ingots and castings made in 1909 were about 182,000 tons of alloyed steel, of which 159,000 tons were ingots and 23,000 tons castings. Of the total of 182,000 tons approximately 42,000 tons were made in Bessemer converters, 120,000 tons in open-hearth furnaces and 20,000 tons in crucible, electric or special furnaces.—*From "Iron Age," May 26, 1910.*

**Air Nitrate Fertilizers.**—Consul-General Frank H. Mason, of Paris, writing of the production of nitrogen from the atmosphere and its use for economic purposes, especially as a fertilizer in agriculture, says that as thus far developed in Europe it is a direct sequel to the manufacture of calcium carbide by the application of electric heat to lime and carbon. He continues:

"When this process was discovered some years ago it was assumed that acetylene gas, generated from calcium carbide, would largely supplant coal gas and revolutionize the existing system of artificial lighting. The first essential requisite for carbide production was abundant and cheap electric current, and extensive

plants were erected along water courses of Europe and preparations made to supply a large and steadily increasing demand.

"But it was soon found that acetylene gas was a difficult and, under certain conditions, a dangerous element to manage; its use became restricted to certain locations and conditions, and experience proved that the combined carbid factories had a capacity of about 100,000 tons in excess of the normal demand for that material.

"About this time Frank and Caro, two German chemists, invented a process through which, by combining nitrogen gas with calcium carbid at a temperature of  $1,000^{\circ}\text{C}$ ., they could produce a combination of lime, carbon, and nitrogen—in other words, a synthetic nitrate of lime—to which they gave the name of cyanamid of calcium, now commonly known as cyanamid, which contains from 15 to 20 per cent. of nitrogen, 60 per cent. of lime, and has qualities as a fertilizer similar to sodium nitrate, or Chilean saltpeter. This process was patented in all countries and became the property of a corporate company, with headquarters at Rome, and known as 'La Société Italiana per la Fabrication de Prodotti Azotati.'

"The calcium carbid therefore was ready, the process for converting it into cyanamid by combination with nitrogen was perfected, and it only remained to provide an adequate supply of atmospheric nitrogen at a moderate cost. This requirement was met by a process invented by Dr. Carl von Linde, of Munich, which was patented in both France and the United States. By this process atmospheric air, having been first liquefied by compression, is subjected, by subsequent expansion under pressure, to a process of fractional distillation, by which the nitrogen is separated, leaving as a by-product oxygen of 50 to 60 per cent. purity, which can be used by burning in the electric arc (sparking) for the manufacture of nitrates and nitric acid. [A copy of the French patent for the Linde process is on file in the Bureau of Manufactures.]

"The cycle was now complete, and it is through the combination of these two processes—the Linde method for recovering atmospheric nitrogen and the Frank-Caro method of combining nitrogen with calcium carbid for the production of cyanamid of calcium—that European progress hopes to provide for the future an adequate supply of nitrate fertilizer for agricultural purposes."

*Activity of German Chemical Factories.*—Deputy Consul-General Simon W. Hanauer, of Frankfort, notes that Germany's chemical industries have in the first four months of this year increased their exports by about 25 per cent., compared with the corresponding period of last year, the values being \$55,700,000 against \$43,800,000. In spite of the higher tariff rates under the new law, the exports to the United States have not diminished. So far, the profits exceed those of last year, while stocks of goods are lower. The new chemical factory at Heyden is competing strongly with the Badische Aniline and Soda Works in the sale of synthetic indigo; the factories producing tannin and other tanning stuffs are competing lively with each other. The works manufacturing artificial fertilizers have already adversely felt the competition coming from the sale of nitrate preparations extracted from the air. The latter will soon be available in large quantities for the world markets, as the large plants which have been in course of erection in Norway are nearing completion.

*Production of Calcium Carbide.*—Consul-General Richard Guenther, of Frankfort, reports the world's production of calcium carbide in 1908 as amounting to 200,000 tons, one-fifth of which was produced in the United States and Canada. The production in the other countries was as follows, in tons: Italy, 32,002; France, 27,000; Norway, 25,000; Switzerland and Austria-Hungary, 20,000 each; Sweden, 12,000; Germany, 9,000; England, 800. There were 70 factories employed in the manufacture of the article. The production has increased very much in recent years.

Consul-General Richard Guenther writes from Frankfort that the Deutsche Gold and Silber Scheide Anstalt, capital, 10,000,000 marks (mark = 23.8 cents), reports 5,803,500 marks net profits for its fiscal year 1909-'10, of which 36 per cent. was paid in dividends. The company's Frankfort factories produce ceramic colors, synthetic indigo, and other chemicals, and its new cyanide and electrochemical works have yielded good results. Its enterprises in the United States, the Roessler & Hasslacher Chemical Company and Niagara Electro-Chemical Company, increased their profits, while its chemical works at Perth Amboy, N. J., earned less, owing to competition.



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## EDITORIALS.

### THE WORKS LABORATORY.

ON a summer journey the writer arrived at a well built paper mill situated on a river in a town of some 12,000 people. The river had been diverted from the rapids through which it once ran and was dammed to furnish power with a head of 20 feet. Electrical power was brought from another power plant situated on a rapids 8 miles below. The mill was of considerable capacity and its sulphite towers prominent landmarks for some distance. Inquiry was made for the chemical laboratory. The first three men asked had never heard of it. A foreman said it was in the sulphite department. Further inquiry developed the fact that it was up three flights of stairs in the tower. Up five flights the cooker was found standing near the digesters. Yes he knew the chemist but he was out to lunch—would be back soon. The laboratory proved to be a small room the size of a closet on the stair landing, and had been passed unidentified. It was within a few feet of one of the digesters, was extremely warm and badly ventilated. Apparatus was all but lacking. Standard solutions were bought in Chicago and diluted for use. One man had scarce room to turn around in this laboratory, two could not possibly have worked in it. An ordinary business man's desk

could not have been placed in it if it were otherwise empty. The cooker explained that the chemist was not a "real chemist" but one who had "just picked it up." It seems he had learned the art from somebody who himself had learned it from a chemist. "We do not do much testing here" said the cooker. "I do some of it myself. Now there's a mill 100 miles from here where they test everything. They test the coal, and the sulphur and the rock and the water, besides the liquors. But we only test the liquors. We get along all right." The chemist did not return. It was time to go. Eight miles down the river the odor of sulphur dioxide was easily detected.

What is true of this paper mill is true of thousands of manufacturing plants throughout this country with this difference: some plants have no chemist at all and no testing apparatus. What is true of this country is true of all countries to a greater or lesser extent. Even in Germany there are many plants chemically uncontrolled, working empirically, by formula. It should not be difficult to demonstrate that in nearly all cases a chemical laboratory pays and pays well. This point has been learned these many years by all progressive superintendents and managers. The difficulty seems to lie in the question: Can a given plant be operated without a laboratory? The cost of a laboratory (although small) shows conspicuously on the books. The profits made possible by a laboratory are lost among other figures unless a special search is made for them. Under these circumstances men of little insight will continue to operate their plants without proper scientific control, until by the competition of better managed plants they are forced to adopt modern methods or go out of business.

In reassuring contrast to the plant with inadequate laboratory and equipment or with none at all stand such establishments as the General Chemical Company, the Solvay Process Company, the Illinois Steel Company, the Galena Signal Oil Company, the Chicago Packing Houses, Parke Davis and Company, the Du Pont de Nemours Powder Company and many others, with their excellent and adequate laboratory equipment and staff. These are all large works and the question may fairly be asked, is not the size of the plant the determining factor in deciding whether a chemical laboratory is a profitable investment? It would not be safe to conclude that the large plant or corporation could afford the expense of a laboratory

while the small one could not. Possibly if a census were now taken the data would show that the investment and expenses for laboratory in the majority of large manufacturing plants were greater per unit of capitalization than in the small ones. Again there are other ways of meeting the issue. If the expense of a chemical laboratory should appear too great, at least a superintendent with thorough chemical and technical training could be obtained. Again the commercial laboratory doing business on a yearly contract basis could be consulted. The intelligent observer of today is again and again forced to conclude that there is now no excuse for a manufacturing plant to operate without adequate scientific and technical control.

## ORIGINAL PAPERS.

### THE NEUTRALIZATION AND FILTRATION OF SMELTER SMOKE.

By W. C. EBAUGH.

Received August 1, 1910.

In the *Journal of the American Chemical Society* for July, 1907, there appeared a series of articles dealing with various phases of the smelter smoke problem, and presenting the matter from points of view that were quite different from one another.

In one of the articles special stress was laid upon the method of measuring the velocities of gases and determining the quantities of solids sent out of a stack during a given time. The results were startling to one who had had no previous experience in work of that kind, and probably awoke a new train of thought in the minds of all concerned with the problems of economic smoke handling and treatment.

A second article pointed out the damage that could be done by even small quantities of sulphur dioxide in the atmosphere, if present a large amount of the time, and cited experiences in many fields to bear out the statements made. The effects of arsenic escaping with the smoke and of copper bearing water issuing from a metallurgical plant also received attention.

The third article dealt with a comparison of the action of gaseous and solid emanations from smelters, and tried to show that although the damage done to crops by sulphur dioxide in certain climatic conditions might be enormous, nevertheless in the dry atmosphere of the intermountain west perhaps the importance of the gases in producing damage might have been overestimated, and the importance of the solid emanations might have been underestimated. The rôle of the solid emanations in injuring stock had already been acknowledged, but its importance in causing injury to vegetation had not been given the attention that it merited.

As the result of litigation long drawn out, in 1906 four smelters in the Salt Lake valley were enjoined from operating, the court decreeing that in order to

be considered harmless a smelter should treat ores that in their natural state contained not to exceed 10 per cent. of sulphur. To comply with such a condition was a commercial impossibility, and a petition that the smelters be allowed to mix ores in such a way that the average sulphur content should not exceed 10 per cent. was presented to the court, but the petition was denied. On appeal the circuit court affirmed the decision of the district court in all material points. Two smelters then went out of commission. A third entered into an agreement with the plaintiffs to filter all the solids from its blast-furnace gases and to send its roaster gases through some 1800 feet of Monier flue and a cooling and expansion chamber of specified construction, and a modification of the injunction was therefore permitted by the court in the case of this party to the suit. The fourth smelter went at the matter somewhat differently, and as a result of many months of experimenting evolved a system for neutralizing the gases from its devices other than blast furnaces in such a way as to permit their filtration. When their plans had been perfected the case was reopened before the district court, and upon the showing made permission was granted to try the new scheme. In other words the injunction was suspended, but not removed.

More or less full accounts of the modifications used have been published in the local press as well as in the technical periodicals, our own *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY* having an article upon the subject in its issue for October, 1909. A brief résumé of that article may not be out of place. It was shown that the gases coming from lead blast furnaces and from zinc plants had been filtered successfully for many years, but that roaster and other gases were not amenable to such treatment. The reasons for the latter statement are (1) that the temperature of gases coming from roasters is so high as to make the cooling of the gases before filtration impracticable or at least unprofitable; (2) that such gases contain more sulphur trioxide than do those from lead and zinc furnaces, and therefore corrode the bags very rapidly; and (3) that finely divided carbon and fume coming from roasters of the ordinary types seem to result in frequent cases of spontaneous combustion in the bag house, with consequent loss of efficiency and greatly increased cost of operation. Messrs. Sprague and Rhoades found that it was possible to prolong the life of a bag indefinitely if the gases led into it were first neutralized with zinc oxide. Experiments upon a larger scale were then conducted, and as a result they proposed to neutralize all the gases coming from a lead plant, roasters as well as blast furnaces, and filter the cooled mixture through bags. The plant was remodeled accordingly, and has now been in use for about two years. The success that has attended its operation under the new plan of operation

has given great satisfaction to all concerned. Looking at the plant one would think that it was out of commission, or at least running only a battery of ordinary steam boilers, for the only stacks that seem to be in use are those on the power house. Prior to the changes the vegetation in the neighborhood of the plant was always more or less injured by products thrown off by the smelter, but repeated examinations of these same districts during 1909 and 1910 have failed to disclose any damage that could be detected by the casual observer. The latter part of the summer of 1909 was unusually wet, and the spring and summer thus far this year have been unusually dry and hot, but the surrounding country has never looked better, according to impartial observers, than during these two seasons.

After the lead plant had been in operation for some months the court granted permission to start the copper plant under similar restrictions, but the company has not taken advantage of this decree. Failure to do so is to be attributed more to economic than to technical or metallurgical causes.

That the improved state of affairs is really due to the changed methods of operation rather than to climatic or other conditions is shown by the fact that other plants working on a similar scale to the one herein referred to, but without such efficient filtration for all gases, have not been surrounded by an unharmed area. Since sulphur dioxide and other flue gases are thrown off into the air in all cases, and only the solids are retained by filtration, it seems that there is some connection between the solids emitted and the damage inflicted upon vegetation, thus affording proof for the conclusions offered in one of the papers printed three years ago.

At best the results given in this paper can be taken only as a "report of progress." Theoretically and practically the escape of sulphur dioxide into the air constitutes an economic waste in the broad sense of the term, and were it possible to convert this gas into sulphuric acid and find a market where it could be utilized directly or indirectly at even a small margin of profit, a new and better method of disposing of this smelter waste might be introduced. At present, however, such a plan appears to be impracticable. Figures taken from the United States Census for 1900 and from various trade reports formed the basis for a calculation made several years ago, that showed that the smelters of Utah alone would be able to make more sulphuric acid than was consumed in the whole United States. If to this enormous output be added that obtainable from Montana, Arizona, California, Washington and other smelting states, the magnitude of the undertaking could be appreciated. The matter of freight rates from smelting districts to localities in which there is manufacturing on a large scale must also be taken into account. It would seem

that for the present at least filtration of smelter smoke offers a partial solution of the problem, but that a better means of avoiding damage may be evolved in the future. Most of us who are still in our youth can remember how the rivers near gas works were polluted by tar and other refuse, how certain industrial plants used to belch out great clouds of black smoke twenty-four hours of the day, and how slaughter-houses treated as waste much of the material that they now turn into profit. Is it too much to hope that changed conditions as exemplified in the gas works, power houses and abattoirs just mentioned may be tokens of what may occur to smelters in the not very distant future?

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SALT LAKE CITY.

### EFFLORESCENCE ON BRICK WORK.

By A. F. GREAVES-WALKER.

Received August 3, 1910.

Wherever brick are used for building purposes, brick walls will be noted which are covered or partially covered with a film of scum. This scum is generally white but may be yellow or green.

It appears at its worst on red brick walls, but may be seen more or less plainly on brick of any color.

When the walls are new it appears as white blotches at various places. Later it may come out all over the building, giving the brick work a faded or dirty appearance. In a few years a red brick building so affected will take on a faded pink appearance which will stay with it forever.

The scumming is always worst near the eaves and downspouts, and under the window-sills and water table. This is caused by leakage of rainwater between the roof and trough and from the downspouts, and through the catching of the water by the sills and water table which consequently soaks into the brick beneath.

The scum is simply a film of soluble salts carried from the interior of the brick to the surface by the water which they absorb, and left there after it evaporates.

This scum is generally composed of sulphates, although it may be composed of any other soluble salt. Chlorides are found in seacoast clays and alkalis in clays of the Western arid region.

In the clays of this country, the scum causing salts, in order of their abundance are:

CaSO <sub>4</sub>	calcium sulphate.
MgSO <sub>4</sub>	magnesium sulphate.
K <sub>2</sub> SO <sub>4</sub>	potassium sulphate.
Na <sub>2</sub> SO <sub>4</sub>	sodium sulphate.
FeSO <sub>4</sub>	ferrous sulphate.
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	aluminum sulphate.

Often all of these occur in a single clay, especially if it has been weathered and subjected to the attack of decomposing pyritiferous minerals.



All of the above salts are very soluble except calcium sulphate, which is soluble 1 : 400. But this is great enough to completely ruin face brick in which it occurs, as the surface is small in comparison with the weight. This particular salt, in fact, is probably responsible for half the ruined walls in this country.

The sulphates of soda, potash, and magnesia will often cause scum when present in the most minute quantities. As little as 0.01 per cent. of any one of these salts has been known to ruin face brick.

There are four ways in which salts are incorporated into the brick:

- (1) Soluble salts in the clays or other materials used.
- (2) Soluble salts in the water used for tempering the clay.
- (3) Soluble salts formed in kilns by oxidation of minerals in clay, or by reaction of sulphurous kiln gases on clay.
- (4) Soluble salts introduced into brick after burning, principally from mortar.

A great majority of clays contain soluble salts, some large quantities, others but a trace. Surface clays are more likely to have a high content than the older deposits. Trouble is encountered in all parts of the world from this source.

Probably 75 per cent. of the scumming comes from this cause.

Often materials are mixed with clays that carry soluble salts into them. Examples of this are the brick made around London, England, in which ashes are used to reduce shrinkage, and brick made along the Hudson in which coal slack is used to aid in burning. In both of these cases the soluble salts in coal add to, if they do not entirely produce, the scum.

In clays that vitrify scumming can be overcome by burning them to a vitrified body, in which case the salts form silicates and become harmless.

The water used for mixing and tempering mud brick often contains soluble salts. This, of course, produces the same effect as if the clays contained them. Many good clays are injured in this way.

The formation of soluble sulphates in the kiln is a very common trouble. It is often encountered with clays that contain practically no troublesome ingredients before being fired.

In many cases there is really no excuse for trouble at this stage. It is simply a case of ignorance on the part of the brickmaker or poorly designed kilns and stacks.

When a kiln is set and the heating up process started, the ware contains considerable moisture. If good judgment is used and the fires are kept at such a stage that only so much of the moisture is being driven off as the sluggish draft of a cool stack will carry off, trouble is not likely to occur; but if the moisture is driven off more rapidly than the stack can handle it, it is precipitated on the ware again, when it absorbs

sulphur from the gases and forms sulphuric acid. This acid attacks the carbonates and other less soluble salts and forms soluble sulphates.

There is no doubt that considerable trouble is caused by the mortar in which the brick are laid. Poorly mixed mortar is dissolved by the rain water and the salts carried into the brick, only to be brought to the surface later. It is therefore always important to take great care with the mortar.

*Methods of Overcoming Scum.*—Many methods are employed to overcome or prevent scum. It is possible to do this in nearly every case, but is often impossible on account of the low selling price of the ware. Where facing brick or other wares are made by the wet process or the ware is vitrified there is practically no excuse for trouble.

The preliminary treatment is the principal method of overcoming or preventing scum. This is done by treating the clay or treating the water used.

*Treating the Clay.*—Clays that contain soluble salts can be washed before using and the salts leached out. This may be done by treating piles of clay, after mining, with water and then allowing them to dry. This method is only possible where high-priced ware is made. Clays are often allowed to stand in piles for from six months to a year, in which case the rain and snow do the same thing.

In many clays the above methods will only cause the trouble. This would be the case where a clay did not contain soluble salts originally, but upon exposure to the weather insoluble salts were converted into soluble salts. This would be the case with pyritiferous clays.

Chemical treatment is very often resorted to. This is accomplished in clays made up by the wet process, by adding, to the water used, such chemicals as will precipitate the soluble salts and form harmless by-products, such as  $\text{BaSO}_4$ . Barium salts are the favorites with which to accomplish this reaction, but others can be used. Barium chloride and carbonate are most commonly used. When these barium salts come in contact with soluble sulphates, barium sulphate is formed, which is practically insoluble in water.

In case soluble sodium compounds are present, the addition of the above-mentioned barium salts would form either  $\text{Na}_2\text{CO}_3$  or  $\text{NaCl}$ , both of which are soluble. However, they are so soluble that they would be readily washed from the surface of the ware by the rain, as soon as they formed.

According to Gerlach, a clay containing 0.1 per cent.  $\text{CaSO}_4$ , which is 0.4 gram per pound, would require 0.6 gram of  $\text{BaCO}_3$  to perform the reaction. However, 6 or 7 grams should be added to every pound of clay, for safety. This would mean practically 100 pounds per 1000 brick. If  $\text{BaCl}_2$  is used, but 26 pounds are required per 1000 brick. However when

BaCl<sub>2</sub> is used, close to the theoretical amount must be added, for if added in excess it will form a scum itself.

This method cannot, of course, be used in the dry press process, where no water, or at least very little, is added, as the barium or other salts must be used in solution to do the required work.

*Treating the Water.*—When it is necessary to use a water that contains injurious soluble salts, it is simply necessary to precipitate them before adding the water to the clay.

Many good clays are being ruined by bad water, when it needs but a few hours of a chemist's time to rectify the trouble.

*Preventing Scum by Correct Drying.*—Scumming is often caused by incorrect drying of the ware. If ware containing soluble salts is placed in a drier and allowed to sweat slowly, the chances are all in favor of scummed ware, whereas, if the water is carried away from the surface of the ware as fast as it appears this will not often be the case.

It is a remarkable physical fact, not yet fully explained, that where a clay contains soluble salts, they are not deposited on the surface at all, or at least to a less degree, where the drying is steady and rapid, than where it is slow and discontinuous. It seems that rapid drying causes the water to come through the pore channels of the clay as through a filter and a sort of osmosis is set up, by which the saline matters are retained inside the mass of the clay, while the water escapes as vapor from the outside. But where the drying is slow the salts get through this barrier and arrive on the surface plentifully.

It is therefore only necessary that brickmakers, in order to avoid trouble from this source, build good driers and instal in them hygrometers by which their operation can be controlled.

Many other methods are used to prevent this trouble. Some of them, however, have but temporary effects.

One of these is to paint the surface of the scummed ware with oil, which for the time being covers up the scum. This is really practicing a fraud, for while the ware does not show scum when put into the building it shows up as soon as the oil evaporates.

Another method is to paint one surface of the unburned brick with a heavy oil or tar. This prevents evaporation from that surface, the salts being carried to the other surfaces. The oil or tar is burned off in the kiln, leaving a clean face. This, too, is only temporary unless the brick is vitrified, as otherwise the salts will be drawn to the clean surface after a few soakings.

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## THE ELECTROLYTIC DETERMINATION OF ZINC IN ORES.

By GEO. KEMMERER.

Received July 30, 1910.

The investigation was undertaken to ascertain if

the zinc content of an ore could not be accurately and quickly determined electrolytically.

The original plan was to separate the zinc from the other constituents of the ore, as zinc sulphide, by a method similar to the "Modified Waring;" this sulphide was then to be dissolved in a little acid, the hydrogen sulphide boiled out, made alkaline with sodium hydroxide and electrolyzed.

Numerous experiments with an ore of known zinc content, using an electrolyte containing from 7–10 grams of sodium hydroxide, gave high non-concordant results.

About this time E. B. Spear, E. E. Wells and B. Dyer<sup>1</sup> showed that several methods gave high results and Spear<sup>2</sup> stated that the high results were due to zinc oxide or hydroxide deposited with the zinc and suggests that a strong alkaline electrolyte might prevent this, but proved that it is theoretically impossible to deposit all the zinc from such an electrolyte. Harrison Hale<sup>3</sup> determined the zinc content of a pure blend, using an electrolyte containing 15 grams of sodium hydroxide. His results were not high and the average of a large number of determinations was very close to the gravimetric results.

*Experimental.*—The electrolytic cell used consisted of a cylindrical nickel gauge cathode which fitted loosely into a 150 cc. Jena beaker, and a revolving propeller-shaped anode.

The cathode surface was about 160 sq. cm. while the anode was rotated about 600 times per minute.

Weighted pieces of C. P. zinc were dissolved with nitric acid in a 180 cc. flask, 2 cc. of sulphuric acid added and evaporated to dense fumes of sulphur trioxide. After cooling, the contents of the flask were rinsed into a 150 cc. beaker, diluted to 100 cc. and stick sodium or potassium hydroxide added. This heated the solution nearly to boiling and it was electrolyzed at once.

When the deposition was complete the cathode was removed without opening the switch and plunged into a large beaker of water. It was then dried with absolute alcohol, and ether, which had been distilled over sodium, heated to 70–100°, cooled and weighed at once.

The gauze electrodes cool quickly and it is important to weigh at once for on standing the deposits gain in weight.

	Weight of deposit.	Weight after standing in desiccator.	Gain.
1.....	0.2501	Over night.....	0.2505 0.0004
2.....	0.2500	Two hours.....	0.2504 0.0004
3.....	0.2517	One hour.....	0.2521 0.0004

After the electrolysis the solution remaining was always tested for zinc by acidifying with dilute sulphuric acid, cooling to 60° and adding 50 cc. of 10 per cent. solution of potassium ferrocyanide. This test

<sup>1</sup> *J. Am. Chem. Soc.*, **32**, 530.

<sup>2</sup> *Ibid.*, **32**, 533.

<sup>3</sup> Thesis, U. of P., 1908.

as shown by E. B. Spear, E. E. Wells and B. Dyer<sup>1</sup> was found to produce a turbidity with 0.5 mg. of zinc in 200 cc. of solution.

After weighing the deposits, the zinc was dissolved from the nickel cathode in 2-3 per cent. sulphuric acid. By this treatment the cathode loss was kept below 0.5 mg., but it gradually darkened due to a trace of lead in the zinc. After ten to twenty determinations the black deposit was removed by pouring a little nitric acid over the electrode.

With an electrolyte containing from 7 to 10 grams of sodium hydroxide the results ran as much as 0.9 per cent. high and were not concordant.

When the alkali was increased to 20-25 grams the following results were obtained:

	A.	V.	Time.	Zinc taken.	Zinc found	Error.
1.....	6	4.4	15	0.1762	0.1759	-0.0003
2.....	6	4.2	15	0.2099	0.2019	0.0000
3.....	5	3.8	15	0.3180	0.3184	+0.0004
4.....	5.2	3.8	15	0.3740	0.3743	+0.0003
5.....	5	4.0	15	0.2412	0.2410	-0.0002
6.....	5	4.0	10	0.2502	0.2501	-0.0001
7.....	5	4.2	14	0.2502	0.2500	-0.0002
8.....	5	4.2	15	0.2502	0.2496	-0.0006
9.....	6	4.4	20	0.2149	0.2147	-0.0002
10.....	6	4.4	20	0.2149	0.2144	-0.0005

The deposits were all a beautiful bluish white and in every case the remaining solution showed no zinc present by the ferrocyanide test.

These results seem to justify the application of the method to ore analysis, so a simple carbonate ore was chosen, the zinc content of which had been determined several times before this work was started. It contained 42.35 per cent. zinc, 9 per cent. iron, no lead. It was treated by the modified Waring method given in Low's "Technical Methods of Ore Analysis" as follows:

"After decomposing the weighed sample by acids alone, or aided by fusion, as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively, or by two evaporations with sulphuric acid, finally to abundant evolution of SO<sub>3</sub> fumes. Dissolve the mass in 25-40 cc. of water and add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminum and boil 10 minutes, or to complete reduction. Filter and wash through a filter containing a piece of aluminum into a beaker containing a stirring-rod or strip of the same metal, cool, add a drop of methyl orange, and neutralize carefully with sodium bicarbonate to a light straw color. Add, dropwise, dilute formic acid (20 per cent. strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, 1 part strong acid to 5 parts water, may be substituted for formic acid when ammonium thiocyanate is to be introduced.) Dilute to about 100 cc. for each 0.1 gram of

zinc possibly present, add, if much iron is present, 2-4 grams ammonium thiocyanate, remove the strip of aluminum, heat nearly to boiling, and saturate with hydrogen sulphide. Allow the pure white zinc sulphide to subside for a few minutes, then filter and wash with hot water."

The zinc sulphide was carefully washed with hot water and dissolved on the filter in a little hot dilute hydrochloric acid. To this solution in the 400 cc. beaker in which the sulphide was originally precipitated 2 cc. of sulphuric acid were added and the whole allowed to evaporate until most of the sulphuric acid was driven off. The zinc sulphate was then rinsed into a 150 cc. beaker diluted to 100 cc., 25 grams of sodium hydroxide added and electrolyzed.

The nickel gauze cathode previously described was used and a current of 6 amperes at a pressure of 4.4 v. was allowed to flow for 15 minutes, while the anode revolved about 600 times per minute.

The results were concordant, but always about 0.3 per cent. high.

Several of these deposits were dissolved, the iron determined colorimetrically and found to be equal to 0.0014-0.0016 gram of iron. When using a 1/2 gram sample of ore this would equal 0.3 per cent.

The sodium hydrate was carefully tested and did not contain more than a trace of iron, so that this large amount must have been carried down with the zinc sulphide.

After numerous experiments it was determined that if 4-5 drops of concentrated hydrochloric acid in place of 5 drops of 1-6, were added to the neutral solution before precipitating the zinc sulphide, that in the presence of ammonium sulphocyanide all the zinc was precipitated as sulphide free from iron.

With this modification the ore containing 42.35 per cent. of zinc, gave the following electrolytic results:

Weight of ore.	A.	V.	Time, min.	Zinc found.	%.
0.5000	5	3	15	0.2116	42.32
0.5007	6	4.2	15	0.2114	42.22
0.4995	6	4.2	15	0.2107	42.18

Average, 42.24

The next ore was a standard sent out by the New Jersey Zinc Company. The results by various chemists ran as follows: 35.5, 35.57, 35.5, 35.2, 35.5, 35.67, 35.87, 35.7; average, 35.56.

#### ELECTROLYTIC METHOD.

Wt. ore.	A.	V.	Time, min.	Zinc found.	%.
0.5002	6	4.2	15	0.1792	35.83
0.5003	6	4.2	15	0.1783	35.64
0.5002	6	4.2	15	0.1794	35.86
0.5009	6	4.2	15	0.1790	35.73
0.5007	6	4.2	15	0.1790	35.77

Average, 35.77

Each of these deposits was tested for iron and not more than a trace was found.

<sup>1</sup> J. Am. Chem. Soc., 32, 530-3:



All the results obtained for this ore included those corrected for iron are as follows:

35.73; 35.74; 35.74; 35.57; 35.67; 35.83; 35.64; 35.86; 35.77; average, 35.73.

#### CONCLUSIONS.

This work has proven that zinc can be accurately determined electrolytically; that the results are not high if the electrolyte contains from 20–25 grams of sodium hydroxide and with a current of  $N. D_{100} = 3.1$  A, all the zinc can be deposited; that this method which is shorter than the usual gravimetric procedure gives results fully as accurate.

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### THE DETERMINATION OF FREE ACID IN HYDROGEN PEROXIDE SOLUTIONS.

By LINWOOD A. BROWN.  
Received July 25, 1910.

Sometime ago in the examination of drug samples, I had occasion to analyze practically all of the different makes of hydrogen peroxide to be found on the Kentucky market, and one of the determinations to be made in the analysis of this preparation is the determination of the free acid present.

The U. S. Pharmacopeia, which is recognized by both Federal and State Food and Drugs Acts, as the standard for drugs, defines this preparation as being:

"A slightly acid, aqueous solution of hydrogen dioxide, which should contain, when freshly prepared, about 3 per cent. by weight of absolute hydrogen dioxide, corresponding to about 10 volumes of available oxygen."

Among other tests for purity for this preparation, it states that if to 25 cc. of the solution, 5 cc. of tenth normal potassium hydroxide V. S. be added, and the mixture be evaporated to about 10 cc. and 3 drops of phenolphthalein T. S. be added, not less than 2.5 cc. of tenth normal sulphuric acid should be required to destroy the red color of the solution after continued boiling (limit of free acids).

This does not appear at first glance, to be a difficult determination, but after a few trials, we found that it did not yield correct results, and upon examination it developed surprising possibilities for trouble.

Acids occur in hydrogen peroxide solutions for two reasons: first, as an aid in preservation; second, in order to remove the barium from which the hydrogen peroxide is prepared. Sulphuric, hydrochloric, phosphoric, oxalic, benzoic acids, etc., are the acids likely to be present.

Acetanilid is used in a large number of hydrogen peroxide preparations on the market, as an additional preservative.

The official method for determining the free acid was soon found to be unreliable, giving high results, so in order to locate the source of trouble, the author

prepared a 3 per cent. hydrogen peroxide solution, using perhydrol, a neutral 30 per cent.  $H_2O_2$  solution. This perhydrol was tested for sulphuric, phosphoric, hydrochloric, oxalic acids, etc., and was found to be entirely free from such acids.

The 3 per cent. aqueous solution of hydrogen peroxide thus prepared was used as a basis for preparing the following solutions containing known amounts of sulphuric, hydrochloric, phosphoric, and benzoic acids.

*Solution "A."*—This solution was made by adding sufficient sulphuric acid to the 3 per cent. solution of  $H_2O_2$  so that 25 cc. of the solution thus prepared were exactly equivalent to 2.5 cc. of  $N/10$   $H_2SO_4$ , which is the limit of acid allowed in the U. S. P. article.

*Solution "B."*—This was prepared in the same way as solution "A", using hydrochloric acid. 25 cc. of this solution were equivalent to 2.5 cc.  $N/10$  HCl.

*Solution "C."*—Prepared as in solution "A", 25 cc. of which were equivalent to 2.5 cc.  $N/10$   $H_3PO_4$ .

*Solution "D."*—25 cc. of solution were equivalent to 2.5 cc.  $N/10$  benzoic acid. This solution was prepared as a type of the organic acids likely to be met with in some preparations of hydrogen peroxide found on the market.

*Solution "E."*—This solution was prepared by dissolving 0.040 gram acetanilid, m. p.  $114^\circ$  C. (cor.), in a sufficient amount of the hydrogen peroxide solution to make 100 cc. corresponding to  $\frac{3}{16}$  grain acetanilid per fl. oz., the strength ordinarily used in preserving peroxide solutions.

Solution "E" was prepared to determine what effect the presence of acetanilid would have on the methods used. The solutions thus prepared were analyzed by the following methods:

*First Method.*—The U. S. P. method, which was carried out as follows: 25 cc. of the solutions representing 2.5 cc.  $N/10$  acid were treated with 5 cc.  $N/10$  KOH and evaporated in porcelain to about 10 cc., and three drops of phenolphthalein added and the excess of alkali titrated back, using tenth normal sulphuric acid, and boiling.

*Second Method.*—A modification of the U. S. P. method was used as follows: 25 cc. of the solution equivalent to 2.5 cc. tenth normal acid were treated with 5 cc. tenth normal potassium hydroxide and evaporated on a water bath in a large platinum dish, kept covered with a watch glass, to avoid loss by the rapid disengagement of gas until effervescence ceased and all  $H_2O_2$  was decomposed. Phenolphthalein was then added and the excess of alkali titrated back, using tenth normal sulphuric acid and boiling off  $CO_2$  after each addition of acid.

*Third Method.*—25 cc. of the solution, equivalent to 2.5 cc. tenth normal acid, were titrated in the cold, with tenth normal potassium hydroxide, using phenolphthalein as indicator.

By the first method used (U. S. P. method) the result of a large number of determinations ran uniformly high, but erratic, due possibly to one or more of the following factors:

- (a) Absorbed  $\text{CO}_2$  from the air.
- (b) Oxidation of the ethyl alcohol in the phenolphthalein indicator by the undecomposed  $\text{H}_2\text{O}_2$ .
- (c) Oxidation of phenolphthalein to phthalic acid or anhydride.
- (d) Acetic acid liberated from acetanilid by the saponification.
- (e) Any undecomposed  $\text{H}_2\text{O}_2$  acting as an acid.

In the second method we have taken advantage of the well-known property that some metals, such as gold, platinum, etc., have of decomposing hydrogen peroxide solutions catalytically, by substituting a platinum dish for the porcelain with the result that *all* the hydrogen peroxide is decomposed. Then by adding the indicator, and titrating the excess of alkali, boiling off any absorbed  $\text{CO}_2$  after each addition of acid, we eliminate all errors with the exception of saponifying action of the alkali on the acetanilid, and get results that are theoretical, varying in no case more than 0.05 cc. tenth normal acid, from the theoretical amount added, which is well within the limit of error.

By the direct titration method (third method) we find the results just a trifle higher than by the modified U. S. P. method, due possibly to a small amount of absorbed  $\text{CO}_2$  in the solution, but more likely to the acidic nature of the  $\text{H}_2\text{O}_2$  itself.

The results by this method were sufficiently accurate for all practical purposes, with the advantage of greater ease and simplicity. The results are not affected by the presence of acetanilid as in the U. S. P. and the modified U. S. P. methods.

To determine the amount of undecomposed  $\text{H}_2\text{O}_2$  existing after the evaporation in porcelain, as in the U. S. P. method, we took several of the samples and determined the strength of the  $\text{H}_2\text{O}_2$  by diluting the liquid remaining after the evaporation to 250 cc. and determining the amount of  $\text{H}_2\text{O}_2$  by titration with  $N/10$  potassium permanganate.

If calculated back to the original sample of 25 cc. used, the amount of absolute  $\text{H}_2\text{O}_2$  found varied between 1.97 per cent. and 2.21 per cent., showing that very little decomposition takes place when the method is carried out in porcelain.

The  $\text{H}_2\text{O}_2$  thus reaches a concentration, if the liquid be evaporated to 10 cc. each time, of 4.4–5.5 per cent. absolute  $\text{H}_2\text{O}_2$ , which is quite sufficient to exert a considerable disturbing influence on the method.

In the modified U. S. P. method no undecomposed  $\text{H}_2\text{O}_2$  could be detected after evaporating or heating in the platinum dish.

**Conclusion.**—The U. S. P. method as given in the U. S. P. for free acid does not yield trustworthy re-

sults, and it is necessary to decompose all the  $\text{H}_2\text{O}_2$  by heating in platinum.

In both the U. S. P. and the modified U. S. P. methods, acetanilid seriously interferes, acting the part of free acid.

Direct titration in the cold appears to be the most satisfactory method as it gives results that are sufficiently accurate for all practical purposes, is not affected by the presence of acetanilid, and has the advantage of greater ease, rapidity, and simplicity.

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## SEPARATION AND DETERMINATION OF COCAIN AND STRYCHNIN, AND ATROPIN AND STRYCHNIN WHEN THEY OCCUR TOGETHER.

By H. C. FULLER.

Received July 25, 1910.

The alkaloids of the coca leaf and of *nux vomica* and of belladonna and *nux vomica* occur together as the active ingredients of certain classes of medicinal products, and it becomes necessary at times to determine how much of each is actually present. The groups follow each other so closely in their solubilities that no separation based on this property is possible, and one is obliged to employ other means.

It is a well-known fact that the coca bases are readily hydrolyzed by acids and by alcoholic potash and a method for the determination of cocaine in a mixture of its allied alkaloids based on this phenomenon has been recommended by Garsed.<sup>1</sup> This chemist carries out the hydrolysis in alcoholic potash by heating for half an hour over the steam bath using a reflux condenser. It has been determined that the *nux vomica* alkaloids under these conditions are not changed and hence a separation can be effected depending on this difference in behavior.

A liquid drug product containing both cocaine and strychnin is first evaporated cautiously to drive off any alcohol if present and then quickly cooled to prevent the decomposition of the cocaine. If the material is a pill, tablet or powder, it is ground up and digested with alcohol containing a little ammonia, the solvent filtered and the treatment repeated twice more, the combined alcoholic solution being evaporated cautiously and the residue taken up with dilute sulphuric acid and filtered if necessary. To the solution obtained by either of these methods, ammonia water is added in excess and the mixture shaken out three or four times with Prolius' mixture, reserving each portion of the solvent and finally discarding the alkaline aqueous liquid. The solvent solution is then filtered, the filter paper washed with more of the solvent and the filtrate evaporated over the steam bath using a fan, care being taken to prevent the residue from

<sup>1</sup> *Pharm. Jour.*, 1903, p. 784.

being heated excessively. The resulting product is now dissolved in about 15 cc. of dilute sulphuric acid and the acid solution shaken out five times with chloroform, if caffeine is known to be present; if not twice is sufficient. All the chloroform shakings are finally combined, washed once with water and then the chloroform discarded and the wash water added to the acid liquid. Ammonia is then added in excess and the solution shaken out three times with chloroform, the solvent solutions are combined, washed once with water, and the chloroform run through cotton inserted in the stem of the separator, into a tared dish; two small portions of chloroform are then run through the cotton into the dish and the whole evaporated cautiously using a fan, and the residue dried at 80 for a short time and then cooled in a desiccator and weighed. Cocain being volatile the drying must be at a low temperature. As the final portions of the chloroform evaporate, the dish should be rotated and removed from the steam to avoid spattering.

The weight thus obtained will give the combined cocain and strychnin, or if the drug extract was present the combined coca bases with strychnin and brucin. The mixture is then dissolved in  $N/5$  alcoholic potash, using 15 cc. for each decigram of cocain supposed to be present, the solution poured into a digestion flask arranged with an air-tight stopper, the dish washed out with 10 cc. alcohol and finally with 10-15 cc. water. The flask is then stoppered and placed over the steam bath for one hour. At the end of that time the flask is opened, the contents poured into an evaporating dish, washing out the flask with alcohol and water, and evaporated until all the alcohol has been driven off. The residue is then transferred to a separator, using water and chloroform, and the alkaline liquid shaken out three times with chloroform, collecting the solvent in another separator. The combined chloroform extracts are then shaken three times with 10 cc. portions of dilute sulphuric acid, the acid being reserved and the chloroform finally discarded. Ammonia is now added until in excess, and on cooling if much strychnin is present it will come out as a fine crystalline precipitate. The solution is shaken out three times with chloroform, the chloroform extract collected in another separator, washed with water, run through cotton into a tared dish and the solvent evaporated. The dried residue will be found to consist of strychnin or strychnin and brucin.

This same general plan may be followed in separating atropin from the nux vomica bases. The tropeins are readily hydrolyzed and the strychnine and brucin can then be shaken out and finally purified according to the above method.

## VOLUMETRIC DETERMINATION OF POTASSIUM BY THE COBALTI-NITRITE METHOD.

By O. M. SHEDD.

Received June 30, 1910.

The writer, in making some determinations on the fertilizer samples sent this year by the referee on potash of the Association of Official Agricultural Chemists, obtained such interesting results in using the cobalti-nitrite method as modified by Drushel<sup>1</sup> for the determination of potassium that it was decided to publish a summary of them, since they throw much light upon the best conditions for applying this method.

The accuracy of this method has been considerably discussed of late and it has been considered of sufficient importance to have been recommended to the above-named association for coöperative work by the referee on potash and also by the referee on soils.

Drushel in his original article had published some results obtained with this method on fertilizers and recommended it for this purpose, and his method, with a slight modification by Bowser,<sup>2</sup> is the one proposed for study this year. On the other hand, the writer<sup>3</sup> has proposed it in connection with the J. L. Smith method for the determination of total potassium in soils and has obtained very good results in this manner. Later on, further work<sup>4</sup> by the writer and others was presented to the association at its annual meeting last year with the result that this method has been taken up by the referee on soils. Incidentally, it might be of interest to mention that the writer has obtained very good results in using this method on the soils sent this year by the referee on soils for coöperative work.

In the method, as proposed for soils, a change was made in the outline as given by Drushel which, while it may seem of small importance, is very essential in the application of the method. Drushel had recommended that the solution (apparently not restricting the volume) at the proper point was to be slightly acidified with acetic acid and a liberal excess of the sodium cobalti-nitrite reagent added and evaporated to a pasty condition on the water bath. On the other hand, the writer in his article had recommended that the volume should be concentrated to about 5-10 cc. before adding the nitrite reagent. That this is the best condition under which to work will be shown later, and it is not necessary to discuss it here, except in a general way. The nitrite reagent being unstable at room temperature and especially so on heating, the method that completely precipitates the potassium when the reagent is added with the minimum amount of heating, of course, is the one to be preferred. Again, when the dilution is too large, the nitrite reagent is all decomposed on heating before the

<sup>1</sup> *Chem. News*, **97**, 124 (1908).

<sup>2</sup> *This Journal*, **1**, 791.

<sup>3</sup> *Ibid.*, **1**, 302.

<sup>4</sup> *A. O. A. C. Proceedings*, 1909.



potassium salt is precipitated and consequently low results will be obtained. Finally, the potassium salt itself is acted on to some extent by the acetic acid and water present, and while it may precipitate at ordinary temperature, on heating the precipitate will disappear and the solution become pink. Therefore, if at the end of the evaporation there is not an excess of the nitrite reagent present, low results will be obtained.

To illustrate the above points, a few qualitative tests might be given. The potassium salt was made by precipitating C. P. KCl solution cold with an excess of the reagent and washed with cold water by decantation. A portion suspended in water and heated in the boiling water bath dissolved slowly, giving a clear pink solution after about two hours' heating. This solution evaporated on the water bath in a dish left a blue residue. On taking up with cold water acidified with acetic acid, a notable quantity of the yellow potassium salt remained, perhaps about half of the original quantity, and the solution was pink. On repeating the evaporation and re-solution a second and a third time, only traces of the yellow salt remained.

Another portion was suspended in water and divided equally between two test tubes. To one, a few drops of acetic acid were added and the two heated side by side in the water bath. The potassium salt disappeared much quicker in the one containing the acid than in the pure water. This experiment was repeated with the same result.

Another portion was allowed to stand at room temperature in contact with 2 or 3 cc. of water, shaking occasionally. After several days, the water became distinctly pink, showing decomposition of the yellow compound.

Another portion was let stand at room temperature in about 50 cc. of water, with occasional shaking. At the end of a month, all but a trace of the yellow compound had disappeared. On evaporating part of the clear liquid at room temperature over sulphuric acid, there remained a yellow residue, apparently consisting mostly of the potassium double salt, but mixed with pink, needle-shaped crystals, having the appearance of a cobalt salt.

A little of the reagent diluted with 10 or 15 times its volume of water and heated on the water bath soon lost its brown color and became pink, showing complete decomposition of the reagent. An equal portion treated in the same manner, except that several drops of acetic acid were added, underwent the change more quickly. The greater the dilution, the quicker this change takes place.

Upon evaporating the reagent to dryness after diluting with water, as in the above experiment, the mass is distinctly purple in color, and upon adding water there remains an insoluble greenish residue containing cobalt while the solution is pink. The char-

acteristic color of the reagent has entirely disappeared which indicates complete decomposition.

To prove that this greenish substance will have the same effect as the potassium salt, if it should be present, the following tests were made: two 10 cc. portions of the reagent were diluted to 15 times their volume and then evaporated until the contents of one was pasty on cooling. The other was further evaporated until the contents were just dry and firm on cooling. They were then taken up with water, filtered, and treated with permanganate and oxalic acid in the same manner as the potassium salt in the method. The following results were obtained:

Contents on cooling.	N/10 KMnO <sub>4</sub> required in titration.
Pasty.....	1.74 cc.
Dry.....	3.08 cc.

The above results show that if these same amounts of this substance were present in two determinations worked like the above on 0.10 gram aliquots of a potassium salt, the results would be too high to the extent of 1.50 per cent. and 2.64 per cent. K<sub>2</sub>O in the respective determinations.

These tests show that too great a dilution should be avoided, because it decomposes the reagent, and also continued heating in the evaporation should be avoided, because in the final stage of evaporation, the last traces of acetic acid may be expelled and as soon as this takes place, the greenish substance is formed more rapidly than it would be if there still remained some free acid.

To show that the above holds true, two 5 cc. portions of the reagent were diluted to 15 times their volume and evaporated until the volume of one was about 5 cc. and liquid on cooling. The other was evaporated until pasty on cooling. When water was added to both, there was a small amount of the greenish residue in the first, but considerably more in the other.

This source of error could be avoided in the work, if a few drops of acetic acid were added to the solution before filtering, as this readily dissolves this substance and would leave the potassium salt practically pure.

The above experiments show that both the cobalt-nitrite reagent and the yellow potassium compound are decomposed by heating with water and that the change is hastened in the presence of acetic acid.

The samples sent by the referee on potash were three in number, namely, commercial muriate, kainit and a complete mixed fertilizer. The directions called for a study of the cobalt-nitrite method in comparison with the official platinum method. The aliquots recommended for the volumetric method were 0.10 gram for the muriate, 0.5 gram for the kainit and 1 gram for the mixed fertilizer. These aliquots were used in all of the determinations. The directions also called for the volume of the solution to be about

25 cc., when 1 cc. glacial acetic acid and 10 cc. recently prepared nitrite reagent were to be added and the evaporation made.

The referee's directions were followed in the determinations below, the aliquots for the two methods being taken from the same solution. In the volumetric method, the solutions were heated until the contents were just dry and firm on cooling.

OFFICIAL METHOD.		
	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
Muriate.....	0.26025	52.05
	0.25980	51.96
Average .....	0.26005	52.01
Kainit.....	0.06380	12.76
	0.06435	12.87
Average.....	0.06410	12.82
Fertilizer.....	0.04660	4.66
	0.04660	4.66

COBALTI-NITRITE METHOD.		
	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
Muriate .....	0.04928	49.28
Kainit.....	0.05930	11.86
Fertilizer.....	not determined	...

It was apparent that the referee's directions had a tendency to give low results, probably due to the volume being too large when the nitrite reagent was added. To see if an increase of the amount of reagent added at that volume would recover the potassium present, the following determinations were made on the muriate.

	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
10 cc. nitrite added.....	0.04928	49.28
15 cc. nitrite added.....	0.05022	50.22
20 cc. nitrite added.....	0.05125	51.25

The following determinations were made by evaporating the solution to about 5 cc. before adding the acetic acid and nitrite reagent. The reagent was added in various amounts and dishes heated until residues were of the consistency as noted on cooling.

MURIATE.			
Nitrite.	Contents on cooling.	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
10 cc.....	dry	0.05159	51.59
10 cc.....	dry	0.05151	51.51
15 cc.....	dry	0.05223	52.23
15 cc.....	dry	0.05155	51.55
15 cc.....	dry	0.05169	51.69
15 cc.....	very dry	0.05142	51.42
15 cc.....	pasty	0.05142	51.42
15 cc.....	thick paste	0.05159	51.59
15 cc.....	very thin paste	0.05134	51.34
25 cc.....	dry	0.05095	50.95
25 cc.....	pasty	0.05108	51.08
KAINIT			
15 cc.....	dry	0.06280	12.56
15 cc.....	dry	0.06360	12.72
15 cc.....	very dry	0.06230	12.46
15 cc.....	very thin paste	0.06315	12.63
25 cc.....	dry	0.06355	12.71
25 cc.....	pasty	0.06345	12.69

#### C. P. K<sub>2</sub>SO<sub>4</sub>—THEORY, 54.05 PER CENT. K<sub>2</sub>O.

Nitrite.	Contents on cooling.	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
15 cc.....	dry	0.05382	53.82
15 cc.....	dry	0.05347	53.47
15 cc.....	dry	0.05458	54.58
15 cc.....	dry	0.05453	54.53
15 cc.....	pasty	0.05390	53.90
15 cc.....	pasty	0.05399	53.99
15 cc.....	pasty	0.05399	53.99

MIXED FERTILIZER.			
Nitrite.	Contents on cooling.	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
25 cc.....	pasty	0.04680	4.68
25 cc.....	pasty	0.04630	4.63

In following the directions of the referee in the above work, the dishes were heated until the residues were syrupy while hot and just dry and firm on cooling. According to Drushel, this is the best plan to follow, for it thus avoids errors in the continued heating of the residues which will vitiate the results. This was done regardless of the time consumed which was noticed varied in similar determinations and very often with different salts.

After some correspondence with the referee, who stated that the method as outlined by him generally gave satisfactory results in his hands, the writer made some further determinations on the samples and also on C. P. salts. In this work, the referee's directions were followed and also the modification as stated above, whereby the solution was concentrated to about 5 cc. before adding the nitrite reagent. The time consumed in the evaporation after adding the nitrite reagent and the consistency of the contents on cooling after the evaporation was made were also noted. The evaporations were made in casseroles of 750 cc. capacity, except in the case of the kainit, when 400 cc. casseroles were used.

#### REFeree's DIRECTIONS.

MURIATE.			
Time.	Contents on cooling.	Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
45 min.....	thin syrup	0.05187	51.87
45 min.....	thin syrup	0.05226	52.26
45 min.....	thin syrup	0.05179	51.79
45 min.....	thin syrup	0.05145	51.45
		Average,	51.84
40 min.....	thin paste	0.05145	51.45
40 min.....	thin paste	0.05136	51.36
45 min.....	thin paste	0.05104	51.04
45 min.....	thin paste	0.05159	51.59
		Average,	51.36
1 hr.....	dry	0.05119	51.19
1 hr.....	dry	0.05110	51.10
		Average,	51.15
KAINIT			
50 min.....	pasty	0.06300	12.60
1 hr.....	pasty	0.06345	12.69
1 hr.....	pasty	0.06285	12.57
		Average,	12.62
1 1/2 hr.....	dry	0.06275	12.55

#### C. P. KCl—THEORY, 63.17 PER CENT. K<sub>2</sub>O.

liquid about 15 cc. vol.			
		Grams K <sub>2</sub> O found.	Percentage K <sub>2</sub> O found.
20 min.....	cc. vol.	0.05093	50.93
45 min.....	thin syrup	0.06108	61.08
45 min.....	thin syrup	0.06358	63.58
45 min.....	thin syrup	0.06283	62.83
1 1/4 hrs.....	pasty	0.06342	63.42
1 1/8 hrs.....	pasty	0.06325	63.25

The determinations below were made by having the volume about 5 cc. when the nitrite reagent was added and 15 cc. of this were used in each case.

C. P. KCl.			
Time	Contents on cooling.	Grams $K_2O$ found.	Percentage $K_2O$ found.
20 min.	liquid	0.06383	63.83
30 min.	slurp	0.06366	63.66
50 min.	paste	0.06383	63.83
C. P. $K_2SO_4$ .			
20 min.	liquid	0.05401	54.01
30 min.	thin paste	0.05435	54.35
50 min.	thick paste	0.05467	54.67

No reason can be easily assigned why the higher results were obtained on the samples when worked by the referee's directions than those given before, unless it is that the time given to the evaporation is a factor to be considered. In this connection, it might be of interest to note that in the low results obtained before, while following the referee's directions, and in some of the higher results obtained at the same time when the volume was reduced to about 5 cc. before adding the reagent, the same stock of reagent was used. Evidently, these variations were not due to the reagent, but rather to the different volumes of the solution on adding the same. In support of this, reference might be made to the more uniform results which have been obtained where this change has been made in the referee's directions.

From the above work, one must recognize that the evaporation is a point that is to be watched in the working of the method and, in fact, an important point which needs further attention before definite conclusions can be drawn.

To determine what other factors influence the results, first the effect of precipitating in larger volumes with the reagent; second, using old nitrite reagent and finally using more or less acetic acid was tried. Also, the plan was tried of adding the nitrite in two portions at different times in the evaporation in order to more completely precipitate the potassium by maintaining the excess of fresh reagent in the solution.

*Effect of Volume.*—10 cc. of new nitrite reagent were added to 0.10 gram of the sample in the volume indicated, which included the volume of the reagent added. The evaporations were then made in the usual manner. In the case of KCl, the residue after evaporation consisted mostly of the greenish substance already mentioned and only a small amount of the potassium salt.

C. P. KCl.		
Volume including reagent.	Grams $K_2O$ found.	Percentage $K_2O$ found.
200 cc.	0.00377	3.77
A. O. A. C. MURIATE		
100 cc.	0.05533	35.33

To illustrate further what effect the reducing of the volume of the solution before adding the reagent has on the results obtained, those determinations made on the A. O. A. C. muriate according to the referee's directions and also where the volume was further

concentrated to 5 cc. before adding the reagent are given for comparison.

Volume of solution on adding reagent.	Grams $K_2O$ found.	Percentage $K_2O$ found.
25 cc.	0.04928	49.28
25 cc.	0.05022	50.22
25 cc.	0.05125	51.25
25 cc.	0.05187	51.87
25 cc.	0.05226	52.26
25 cc.	0.05179	51.79
25 cc.	0.05145	51.45
25 cc.	0.05145	51.45
25 cc.	0.05136	51.36
25 cc.	0.05104	51.04
25 cc.	0.05159	51.59
25 cc.	0.05119	51.19
25 cc.	0.05110	51.10
Average,		51.22
5 cc.	0.05159	51.59
5 cc.	0.05151	51.51
5 cc.	0.05223	52.23
5 cc.	0.05155	51.55
5 cc.	0.05169	51.69
5 cc.	0.05142	51.42
5 cc.	0.05142	51.42
5 cc.	0.05159	51.59
5 cc.	0.05134	51.34
5 cc.	0.05095	50.95
5 cc.	0.05108	51.08
Average,		51.49

The plan was also tried of adding the nitrite reagent to the dry residue of the salt after evaporation, but on account of the potassium salt being precipitated so finely divided, that it was impossible to filter it, the determination was discarded. This was repeated with the same result.

*Effect of Old Reagent.*—The reagent used here had been made for about eight months and kept in the dark. The referee's directions were followed in the work, except in the last two determinations on the muriate. In these, the volume of the solution was about 5 cc. on adding the reagent.

A. O. A. C. MURIATE.			
Reagent used.	Contents on cooling.	Grams $K_2O$ found.	Percentage $K_2O$ found.
10 cc.	dry	0.03531	35.31
10 cc.	dry	0.03655	36.55
20 cc.	dry	0.05050	50.50
20 cc.	dry	0.05076	50.76
KAINIT.			
20 cc.	dry	0.06085	12.17
20 cc.	dry	0.06095	12.19

In connection with the above work, the following experiments were tried to see if it was possible to determine colorimetrically how much the old reagent had decomposed on standing. Two cc. each of the new and of the old reagents were diluted to 50 cc. in Nessler tubes, and, by comparing the two, it was found that, judging from the color, two-fifths of the old reagent had decomposed.

When the color test was made on the old reagent in the above, the solution had the characteristic brown color of the reagent. After the test was made, the tubes were left standing in the light for about six



hours, and during that time about one hour in the sunlight. At the end of the time, the solution in the tube containing the old reagent had changed to pink, showing complete decomposition, while the new reagent solution was still faint brown, but much lighter in color than before, showing a decided decomposition had taken place. After standing about  $1\frac{1}{2}$  hours longer in the sunlight, this solution also became pink in color.

Evidently, the reagent must be kept in the dark to prevent decomposition.

*Effect of More or Less Acetic Acid.*—The plan followed was to evaporate the solution to about 5 cc. volume, 15 cc. new reagent added and the amounts of acetic acid stated. The contents of the dishes were evaporated until the volume was about 5 cc., when they were taken from the bath. This was done in order to eliminate any error caused by further evaporation.

A. O. A. C. MURIATE.			
Acetic acid.	Contents on cooling.	Grams $K_2O$ found.	Percentage $K_2O$ found.
None.....	thin paste	0.05142	51.42
1 cc.....	thin paste	0.05134	51.34
5 cc.....	pasty	0.05246	52.46

A. O. A. C. KAINIT.			
None.....	thin paste	0.06330	12.66
1 cc.....	thin paste	0.06315	12.63
5 cc.....	pasty	0.06450	12.90

*Addition of the Reagent in Two Portions.*—The determinations below were made according to the referee's directions, that is, by adding 10 cc. new reagent to the volume at 25 cc. The solution was then evaporated to about 5 cc. volume and 5 cc. more of reagent were added. The evaporation was continued until the contents were dry on cooling.

Muriate.....	50.09 per cent. $K_2O$
Kainit.....	12.41 per cent. $K_2O$

In the following experiments, an attempt was made to estimate the potassium by adding the salts which compose the nitrite reagent in separate solutions at the time the evaporation was to be made. In other words, it simply consisted of preparing the reagent in the presence of the potassium salt to be estimated. If found to work, it was thought that this would improve the method, because it would be possible in this way to regulate the volume of the solution, which is important, and at the same time avoid the use of the prepared reagent which decomposes slowly on standing.

For the work 220 grams  $NaNO_2$  were dissolved in  $H_2O$  and made to 500 cc. and designated the sodium nitrite solution. 113 grams of cobalt acetate were dissolved in  $H_2O$  and 100 cc. 50 per cent. acetic acid added (one-half of the amount prescribed) and the solution made to 500 cc. and designated as the acetate solution.

*A. O. A. C. Muriate.*—The solution containing 0.10 gram salt was evaporated to dryness and taken up

with 5 cc. of the sodium nitrite solution and then 5 cc. of the acetate solution were added, but no acetic acid and the whole evaporated until the contents were pasty on cooling. Result, 50.59 per cent.  $K_2O$ .

Another trial was made in same manner, except the acetate solution was added first and then the sodium nitrite. Result, 51.53 per cent.  $K_2O$ .

*C. P.  $K_2SO_4$ .*—The same method as followed in the second determination above was then tried on a solution containing 0.10 gram of the salt, and the evaporation continued until the contents were dry on cooling. Result, 52.43 per cent.  $K_2O$ .

Some further determinations were made on 0.10 gram aliquots of C. P.  $K_2SO_4$  and C. P.  $KCl$  by adding the acetate to the dry residue after evaporation and increasing the amount of acetic acid present to that prescribed in the regular method. In this work, 1.5 cc. of glacial acetic acid and 7.5 cc. each of cobalt acetate and sodium nitrite solutions were added and the evaporations continued until the contents were pasty on cooling. The results obtained were:

C. P. $K_2SO_4$ —	55.10 per cent. and 54.84 per cent. $K_2O$
C. P. $KCl$ —	63.39 per cent. and 63.52 per cent. $K_2O$

The plan of adding the acetate solution first seems to be the most promising one, and further work along this line may prove that this is a safe plan to follow, although as yet there has not been sufficient work done to draw definite conclusions. It is hardly necessary to add here that for the above work, it is better to have chemicals free from potassium, or a blank is all the more essential for work of this kind.

The blank used in all the other work had remained constant and never varied from 0.20–0.23 cc.  $N/10$   $KMnO_4$  solution but the blank here contained too much potassium from the chemicals used, it not being removed as it is in the ordinary nitrite reagent. As no purer chemicals were at hand, this work was discontinued, but it merits further investigation.

According to Bowser,<sup>1</sup> the cobalti-nitrite method for qualitative tests for potassium is much more satisfactory when an equal volume of strong alcohol is added to the solution to be tested. In this manner, he claims that very small amounts of potassium are precipitated in much less time than from an aqueous solution.

From his work, the writer was led into a series of experiments to see if the above could be used for quantitative purposes. If such would prove to be the case, then the evaporation in the method would be eliminated, which would be a great improvement in the work.

*C. P.  $K_2SO_4$ .*—The plan followed at first was to evaporate the solution containing 0.10 gram of the salt to dryness. To the residue was added 5 cc. of the acetate solution and then 5 cc. of the sodium

<sup>1</sup> *Jour. Am. Chem. Soc.*, **32**, 78; *Chem. News*, **101**, 100.

nitrite solution already described. 10 cc. of alcohol were then added and allowed to stand at ordinary temperature for the time indicated.

Time.	Percentage $K_2O$ found.
15 minutes.....	52.20
60 minutes.....	51.99

The next plan tried was to evaporate the solution to about 5 cc. volume and then add 10 cc. of the ordinary nitrite reagent and 15 cc. alcohol. In the first two determinations below, 0.1 cc. glacial acetic acid was added and in the third, no acetic acid. The solution stood at room temperature for the time indicated.

Time.	Percentage $K_2O$ found.
Filtered immediately.....	50.78
5 minutes.....	50.80
15 minutes.....	45.85

In the next experiments, the addition of the alcohol was omitted and the work pursued along a different line. It had been found in working on the A. O. A. C. samples that the addition of more acetic acid than the directions called for had a tendency to give higher results in the regular method.

The plan was then followed of evaporating the solution containing 0.10 gram aliquots to about 5 cc. volume, cooling, and adding 10 cc. of nitrite reagent and the amounts of glacial acetic acid indicated. The solution was then allowed to stand for 30 minutes at room temperature.

A. O. A. C. MURIATE.

Acetic acid added.	Percentage $K_2O$ found.
1 cc.....	48.98
5 cc.....	50.38
15 cc.....	Could not filter

Evidently here, as in the regular method, an increase of acetic acid seems to give a higher result, but whether this increase is due to more potassium precipitated or to other causes is not easy to determine.

It was thought that perhaps the increase of acetates present in the solution influenced the precipitation of the potassium by the nitrite reagent and to prove this, if possible, the following experiments were made on C. P. KCl. Two 0.10 gram aliquots of the salt were taken and to one, after evaporating to dryness, was added 10 cc. of a saturated solution of sodium acetate and 10 cc. nitrite reagent. To the other aliquot, after evaporating to about 5 cc. volume, was added 10 cc. reagent and then 10 grams of sodium acetate. Both were allowed to stand 1 hour at room temperature and gave respectively 55.02 per cent.  $K_2O$  and 48.34 per cent.  $K_2O$ .

To determine if it was possible to completely precipitate the potassium at room temperature by this method, if the volume of the solution was reduced, the following experiment was tried on C. P. KCl.

Two 0.1 gram aliquots were evaporated to about 5 cc. volume, 1 cc. glacial acetic acid and 10 cc. nitrite reagent added and the whole put in a desiccator over  $H_2SO_4$  and the air exhausted as much as possible by means of the suction pump. It was then allowed to stand about 24 hours and at the end of that time, the solution had evaporated and the residue was nearly pasty. Result, 65.74 per cent. and 67.52 per cent.  $K_2O$ .

In every determination that has been made without heating the solution, it has been impossible to wash the potassium sodium cobalti-nitrite with water until the filtrate was colorless. While the washings did not contain any of the precipitate in suspension, they had a yellow color which seemed to indicate that either the salt itself was dissolving, or, which is more probably the case, it was contaminated with some substance which made it difficult to wash clean. While it is easy to understand how low results are obtained while working in this procedure, the high results can only be explained on the supposition above, that the potassium salt contains some other compound that has been formed which is difficult to wash out and reacts with permanganate.

From his experience with the Drushel modification of the cobalti-nitrite method, the writer believes that it is very accurate if properly handled, but an inexperienced worker not knowing its weak points may not have this opinion with his first use of it. Briefly stated, the outline of the method which has given the best and most uniform results in this work is as follows:

The solution containing the potassium salt, after the preliminary work has been done to get it at this stage, is evaporated in a 500 cc. casserole to a small volume of about 5 cc., slightly acidified with acetic acid and 15 cc. fresh nitrite reagent added. The larger amount of nitrite reagent makes possible a better filtration and a good excess of reagent after the evaporation is made. The solution is evaporated on the water bath for about 45-60 minutes, or until the contents become a thick syrup while hot and pasty on cooling. Continued heating is to be avoided, and this is important to obtain good results. After the filtration is made and the casserole washed, the Gooch crucible and contents can be put in the same casserole and treated with permanganate, as prescribed in the method.

In conclusion, the writer desires to express his sincere thanks to Dr. A. M. Peter, of this Station, for the valuable advice he has rendered during the progress of the work.

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LEXINGTON, KY.  
May, 1910.

# A COMPARISON OF BOLLING'S, HARDING'S AND DREHSCHMIDT'S METHODS FOR DETERMINING SULPHUR IN ILLUMINATING GAS.

By E. P. HARDING AND CARL TAYLOR.

Received June 8, 1910.

Randolph Bolling, chief chemist for the Nova Scotia Steel & Coal Co., Sidney Mines, N. S., in suggesting the advisability of ascertaining the total sulphur in suction producer gas, used a wet oxidation method, in which he assumed that all of the sulphur in the sulphur compounds is oxidized to sulphur dioxide. Bolling states that Bunte's method<sup>1</sup> could be used in analyzing illuminating gas which has been more or less purified but that, with unpurified producer gas which contains sulphur in other than simple combinations like hydrogen sulphide and carbon bisulphide, the method would fail to give all of the sulphur. He also states that Drehschmidt's method<sup>2</sup> gives accurate results by completely oxidizing all of the sulphur, but objects to the method on account of the complexity of the apparatus used and the difficulty of keeping the gas burning continuously in the Drehschmidt burner.

The principle of Bolling's method is the oxidation of the sulphur in the sulphur compounds present to sulphuric acid by means of a saturated solution of bromine in hydrochloric acid, and a gravimetric determination of the sulphur by precipitating and weighing it as barium sulphate. The apparatus consisted of a five liter aspirator bottle, a thermometer, barometer and two 500 cc. capacity absorption bottles.

The method in detail is as follows: The aspirator is filled with water and connected with the absorption bottles which are connected to the producer gas main by means of a short length of pipe packed with loose asbestos fiber. The water is allowed to flow slowly from the aspirator, thereby drawing gas through the bromine solutions. The temperature and pressure are taken during the process. The contents of the absorption bottles are transferred to a 750 cc. beaker and the bromine completely removed from the bottles by washing with distilled water. Two grams of sodium carbonate are then added to the solution which is heated to boiling to drive off the excess of acid and water. The sulphur is precipitated as barium sulphate by adding to the diluted hot solution a 10 per cent. solution of barium chloride, and boiling vigorously for thirty minutes. The barium sulphate is then dried, ignited and weighed and the sulphur determined by the following formula,

$$S = 200.0 \ p \ 0.013748 \times \frac{750.8}{283} \times \frac{273}{B-f} = \\ p \ 729.47 \times \frac{273+t}{B-f}$$

in which  $t$  is temperature of the gas,  $f$  the tension of

water vapor at the temperature  $t$ ,  $B$  the barometric pressure,  $p$  the weight of the barium sulphate and  $S$  the amount of sulphur in 100 cu. m. of the gas.

The writers of this paper believed that purified coal gas contains more complex sulphur compounds than suction producer gas made from hard coal in a continuous automatic feed producer. They believed Bunte's method to be more efficient for determining the total sulphur in such producer gas than in purified coal gas. And they doubted the efficiency of Bolling's method as applied to purified coal gas.

This doubt led to determinations of the total sulphur in Minneapolis illuminating gas by both Bolling's method and Harding's modification of Drehschmidt's method and to a comparison of the efficiency of the two methods.

Harding's method and the apparatus used were those described by him in the *Journal of the American Chemical Society*, 28, 537, with the exception that only 0.5 cc. of bromine was used instead of four. Drehschmidt's original method is given in *Chem.-Ztg.*, 2, 1382 (1887). The principle of the method as modified is the combustion of the gas in a specially constructed glass burner within the body of a large retort, in the presence of bromine vapors, the aspiration of the products of combustion with some bromine vapors through a 5 per cent. solution of potassium carbonate, and the precipitation of sulphur as barium sulphate.

The apparatus with the exception of the burner is of the simplest construction and can be set up at once in any working laboratory. This burner eliminates one of Bolling's objections to the original Drehschmidt method.

The Bolling process was slightly modified so that it was possible to run under the same conditions as in the Harding method. Four cylinders of 150 cc. capacity were used, in each of which was placed 120 cc. of bromine water and 15 cc. of concentrated hydrochloric acid saturated with bromine. This gives the gas a longer column of solution to bubble through. The gas was aspirated through by means of a suction pump, after first passing through a wet meter and governor. Gas was drawn through till the first three solutions were nearly decolorized, leaving the fourth only slightly affected. This required about three-fourths of a cubic foot of gas.

In the Bolling method as described only five liters of gas were used. As the Minneapolis illuminating gas is low in sulphur content, and as it was found that in using this amount, a milligram difference in the weight of barium sulphate obtained made a 2 per cent. error it was believed that better results could be obtained by using larger amounts of gas and more absorbent.

In each method the gas was passed through the same wet meter which had been used for several

<sup>1</sup> Bunte, *Journal für Gasbeleuchtung*, 31, 895 (1888).

<sup>2</sup> *Chem.-Ztg.*, 2, 1362 (1887).



years for measuring the illuminating gas for analysis, and through which gas had been passed several days to insure complete saturation of the water.

The amounts of gas used were reduced to standard conditions of temperature and pressure by the following formula:

$$V = V \frac{b - c}{760 (1 \times 0.003635 \bar{T})}$$

The results obtained were as follows:

Date.	Temp.	Press., mm.	Obs. vol.
Jan. 20, 1909.....	20°	748	3/4 cu. ft.
Jan. 30.....	22	745	3/4 cu. ft.
Feb. 9.....	20	741	3/4 cu. ft.
Feb. 18.....	21	743	1/2 cu. ft.
Feb. 27.....	21	744	3/4 cu. ft.
Mar. 2.....	23	744	3/4 cu. ft.

Grains sulphur per 100 cu. ft.

Harding.	Bolling.	Ratio.
9.0360	5.2884	1 : 1.709
10.2302	5.6843	1 : 1.801
7.9555	5.2824	1 : 1.506
8.9620	5.4467	1 : 1.647
8.3041	5.5886	1 : 1.485
9.3067	5.7635	1 : 1.615

Two tests were made, using the original Bolling method to observe if the oxidation was complete in the modified process with the following result:

Date.	Temp.	Press., mm.	Obs. vol.
Feb. 10, 1909.....	24°	745	3/4 cu. ft.
Feb. 10.....	24	745	1/2 cu. ft.
Feb. 11.....	22	743	3/4 cu. ft.
Feb. 11.....	22	743	1/2 cu. ft.

	Grams sulphur per 100 cu. ft.	Ratio.
Harding.....	10.5978	1 : 1.371
Bolling.....	7.7329	
Harding.....	11.0443	1 : 1.264
Bolling.....	8.7352	

These results as compared to the above are within the limits of experimental error showing complete oxidation.

The sulphur content of the sodium carbonate and bromine was not determined but, as much more of each was used in the Bolling method than in the Harding method, if sulphur was present as impurities it would be in favor of the Bolling process.

The same wet meter was used in each process and the same amount of gas used in each determination so that the error of absorption of any sulphur compounds was eliminated.

The solution from the Bolling process gave considerable trouble in concentrating and precipitating the barium sulphate. It was difficult to remove the last trace of bromine and the large amount of bromine present produced bumping difficult to control. It was necessary to evaporate nearly to dryness and dilute the residue very much and it was often necessary to reconcentrate and redilute in order to precipitate the barium sulphate. Carrying the evaporation too far decomposed some of the organic bromide compounds, liberating bromine.

During the process the bromine vapors attacked the rubber connections and tubing, and bromine products were deposited to such an extent in the suction pump as to impair its efficiency.

From these observations it appears that Bolling's process is insufficient for determining the total sulphur in a gas of such composition as Minneapolis illuminating gas.

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## THE NITROGEN AND HUMUS PROBLEM IN DRY-LAND FARMING.

By ROBERT STEWART.

Received July 22, 1910.

The effect of cultivation and the growth of crops upon the nitrogen and humus content of soils has been studied by various investigators, both in America and Europe. In general the results of the various investigators indicate that cropping and cultivation is very destructive to the organic matter and the nitrogen of the surface soil.

Berthelot,<sup>1</sup> in 1886, reported that the carbon and nitrogen content of calcareous clayey soil, originally very deficient, was gradually increasing owing to the action of diatoms.

Deherain<sup>2</sup> found that the soils from plots which had not been manured has lost over 50 per cent. of their carbon. The light soil of Grignon lost nitrogen and the amount lost greatly exceeded the amount removed by the crops. The loss of carbon was due to the oxidation of the organic matter, while the greater loss of nitrogen was due to drainage.

Snyder<sup>3</sup> has found that in the humid section in grain-cultivated soils there is a rapid decline of the vegetable and animal matter, and a loss of the element nitrogen. According to Snyder the nitrogen was lost not only by the removal of the nitrogen in the crop but that drainage and denitrification played a very important part in the loss of nitrogen. Snyder also found that summer fallowing<sup>4</sup> was more destructive to the nitrogen and humus content of the soil than was the continuous cropping to wheat. When summer fallowing was practiced, six times as much nitrogen was lost by other processes as was removed by the plant as food.

Ladd<sup>5</sup> found that long-continued cropping of land with wheat by the fallow process was very destructive to the nitrogen content of the soil.

Alway,<sup>6</sup> in 1909, reported that fields in Nebraska which had been long under cultivation showed a great loss of nitrogen, humus and unhumified organic

<sup>1</sup> *Compt. rend.*, **102**, 951 (1886).

<sup>2</sup> *Ibid.*, **109**, 781 (1889).

<sup>3</sup> *Minn. Exp. Sta. Bulls.*, **30**, **41**, **53**, **65**, **70** and **94**.

<sup>4</sup> *Bull.*, **70**, *Minnesota Exp. Sta.*, p. 260.

<sup>5</sup> *Bull.*, **24**, *North Dakota Exp. Sta.*

<sup>6</sup> *Bull.*, **111**, *Nebraska Agr. Exp. Sta.*, p. 10.

matter. He says: "The greatest losses of organic matter, nitrogen and humus have been caused either by the washing or by the blowing away of the surface soil."

Alway and Vail,<sup>1</sup> in 1909, reported the accumulation of nitrogen in a prairie soil due to the deposition in rifts of organic matter by the wind.

Alway and Trumbull, in April, 1910, reported on the loss of nitrogen in cropped land when compared with adjacent virgin land. They found that the loss of nitrogen, humus and organic matter in twenty-five years was about one-third of the amounts originally present in the prairie soil. In certain cases they found that the content of nitrogen, humus and organic matter in the long-cultivated soil was slightly higher than in the virgin soil, which they attribute to the difficulty of obtaining samples of virgin soil which correctly represented the original composition of the cultivated field. The observed loss of nitrogen, humus and organic matter in the cultivated soil is due to two causes: oxidation of the organic matter and erosion by the wind.

At the same time Bradley<sup>2</sup> reported a study made of the virgin and cropped soils of Eastern Oregon. He found that while the nitrogen content of the soils which had been cropped for about twenty-five years was about the same as that of the adjacent virgin land the carbon content had decreased to a marked extent.

Headden,<sup>3</sup> in February, 1910, reported the accumulation of nitrogen in the form of nitrates in some Colorado soils. This accumulation of nitrogen he believed to be due to the fixation of free nitrogen of the atmosphere by microorganisms.

#### EXPERIMENTAL PART.

In view of the known action of continuous cropping and summer fallowing upon the nitrogen and humus of humid soils, a knowledge of the effect of dry-farming upon the nitrogen and humus of dry-land soils became of exceedingly great importance. With this idea in view the author, in the summer of 1907, had a survey made of the dry-farming area in Cache Valley, the oldest dry-farming district in the State of Utah. Some of the farms of this district have been under cultivation for forty-five years and yield as good crops apparently as they ever did. The important principle of dry-farming is summer fallowing for the purpose of conserving the moisture of the soil. According to all the teachings of the humid agricultural districts as noted above, the practice of this principle, while it conserves the moisture of the soil, is also ideal for the destruction of the organic matter of the soil with the resulting loss of nitrogen.

The survey was started with the hope of learning something regarding the effect of crop production and

summer fallowing upon the humus, nitrogen and nitric nitrogen of the soil. The results obtained were so opposite to the teachings of the humid agriculturists and so significant that the author felt that they should be confirmed by further work before publication. The publication of the recent articles along this same line by other investigators has led the author to believe that these results would be of interest to others working along similar lines. More extended studies of the soils of the dry-farming sections of the State are being made at present, but the results now available are reported.

The soils studied are derived from the near-by mountain ranges, which are composed largely of limestone and quartzite. Cache Valley was at one time Cache Bay of old Lake Bonneville. The erosion of the near-by mountain ranges loaded the mountain streams with finely divided particles of limestone and quartzite, and when the running waters of the streams met the quiet waters of Cache Bay the streams deposited their load. It is of this material that the soils of the dry-farming area of Cache Valley is composed.

The plan of the experiment called for a careful examination of the individual farms of the section and careful sampling in several places of the cropped land and also of the adjacent virgin soil. The soil was sent to the chemical laboratory and the nitric nitrogen determined immediately by the phenoldisulphuric acid method. The moisture was also determined in order to convert results for nitric nitrogen to the dry basis. The samples were then air-dried and preserved for determination of total nitrogen and humus. The total nitrogen was later determined by the Kjeldahl method and the humus determined by the method of the Official Agricultural Chemists.

While the data obtained are insufficient from which to draw sweeping conclusions, there are certain facts which are brought out by the study. The cropping of the dry land to alfalfa has a tendency to cause a decrease of the humus content of the soil and in a majority of cases the nitrogen content also. The cropping of land to wheat, either continuously or by the summer fallow method, has a tendency either to not effect or else slightly to increase the nitrogen and humus content of the surface foot of the soil when compared with that of the adjacent virgin soil.

In Table 1 will be found the results obtained by taking an average of all the determinations made on the wheat, virgin and alfalfa land studies.

TABLE 1.—SUMMARY OF RESULTS.

Results for Total Nitrogen and Humus Reported as Per Cent. of Dry Soil.

Crop.	Depth of sample	No. of analysis	Total nitrogen.	Nitric nitrogen.	Humus.
Wheat.....	0-12	27	0.2055	0.80	2.67
Virgin.....	0-12	22	0.1984	1.04	2.45
Alfalfa.....	0-12	11	0.2009	1.74	2.27

Results for Nitric Nitrogen Reported as Parts Per Million of Dry Soil.

Wheat.....	12-24	24	0.1466	0.76	2.45
Virgin.....	12-24	19	0.1823	1.38	1.99
Alfalfa.....	12-24	11	0.1604	0.60	1.73

<sup>1</sup> THIS JOURNAL, 1, 74 (1909).

<sup>2</sup> *Ibid.*, 2, 139.

<sup>3</sup> Bull. 155, Colo. Agric. Exp. Sta., Feb., 1910.

The nitrogen content of the first foot of the virgin soil is lower than that of either the alfalfa or wheat land. The humus content of the wheat land is slightly higher, while that of the alfalfa land is lower. The nitric nitrogen content varies from 0.80 part per million in case of the wheat land to 1.74 parts in the alfalfa land.

In the second foot the nitrogen of the virgin soil is higher than either the alfalfa or wheat land. The humus of the wheat land is higher than that of the virgin while that of the alfalfa is lower. All three of the constituents decrease with the depth of the samples.

In studying the results given for an explanation of the phenomenon noted there are several explanations which suggest themselves.

In the first place the assumption is made that the composition of the virgin soil now correctly represents the composition of the cultivated soil before the beginning of cultivation. The impossibility of obtaining a sample of virgin soil which correctly approximates the original composition of the soil is obvious. The uniformity of the results obtained on so many samples over such a large district would seem, however, to indicate that this would not explain all of the phenomenon noted.

In the second place a part of the increase in nitrogen in the first foot may be accounted for by causes similar to those which cause the "rise of the alkali" in arid regions. This, however, is hardly probable and if it has any influence at all it would be very slight.

Again it is possible that azotobacter or other micro-organisms which fix the free nitrogen of the atmosphere are in relatively great abundance in our arid soil and fix the free nitrogen of the atmosphere to a relatively great extent. This explanation seems to be the favorite explanation of all observed phenomenon which does not otherwise find a ready explanation from other causes. If such is the case, however, we have not evidence of it and it is somewhat ungenerous to throw the burden of proof upon the shoulders of the bacteriologist. This is a line, however, along which more work should be done with arid soils.

The last and more probable explanation which suggests itself is the following: the method of successful dry-farming for conservation of the limited moisture supply and the demands of the plants for water cause their roots to penetrate to a far greater depth than similar plants in a humid climate. The feeding range of the plant for plant food is thus increased. The plant probably gets a greater supply of its nitrogen from below the first foot than a similar plant would in a humid climate. The wheat also is harvested by a header and practically all of the straw containing nitrogen derived from below the first foot is all added to the surface foot. This greatly increases the nitrogen and humus content at the expense of the lower foot

section. This explanation appears to be probable. It is important to observe in this connection that the nitric nitrogen is somewhat low in all cases, indicating that all of the increase is due to nitrogen in the organic form.

The author wishes to acknowledge his indebtedness to Mr. F. D. Farrell, who made the survey and who made the nitric nitrogen determinations; to Mr. W. L. Walker, who made the nitrogen determinations; and to Mr. F. S. Harris, who made the humus determinations.

#### CONCLUSIONS.

1. The cropping of dry-farming land in the district studied to wheat either by the summer fallowing method or by continuous cropping does not decrease the nitrogen or humus of the surface foot of the soil.
2. The second foot of grain-cropped land contains less nitrogen and humus than does the second foot of the adjacent virgin soil.
3. The cropping of dry-farm land to alfalfa causes a decrease of the humus and in a majority of cases the nitrogen over that of the adjacent virgin soil.
4. The observed phenomenon in case of the grain-cropped land is probably due to the addition of nitrogen to the surface foot from lower depth by the addition of straw which also increases the humus content.
5. This work indicates that in a study of the nitrogen and humus problems in dry-farming, attention must be paid to greater depth of soil than the traditional ploughed surface.

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## NOTES AND CORRESPONDENCE.

### A USE FOR THE GOOCH IN PAINT ANALYSIS.

Recently the writer had occasion to analyze a green pole paint falling under the following specifications: Vehicle, pure linseed oil, 60-7 per cent; benzine, not over 2 per cent.; pigment, 33-40 per cent., made up as follows: graphite, 50 per cent.; gypsum, 35 per cent.; and a mixture of Prussian blue and chrome yellow, 15 per cent.

On attempting to separate vehicle from pigment, much difficulty was experienced owing to the exceeding fineness of the pigment. On extracting with ether in a Soxhlet thimble, as done by Holley and Ladd, the pigment repeatedly passed through the thimble in spite of all precautions. On centrifuging as done by the same authors, there was practically no separation after whirling for three hours at a high rate of speed.

Finally extraction with a succession of solvents, as done by Walker in *Bull. 109*, Bureau of Chemistry, was tried. Here we met with some measure of success, but still the separation was anything but complete, and it occurred to the writer to try the use of a gooch.

A gooch was carefully prepared, using a heavy bed of very fine asbestos; and through this crucible the successive extractions (as per *Bull. 109*) were decanted, using a fairly strong suction. In this manner we obtained a very satisfactory separation where other standard methods had failed.

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## SOME NEW TESTS.

No. 1. *Differentiation of Anhydrous Acetic Acid from Glacial Acetic Acid*.—To the solution to be tested is added a small crystal of selenious acid ( $\text{SeO}_2$ ) or the sodium salt. The latter is in this test preferable.

If anhydrous acetic acid is present a red precipitate of amorphous selenium will be noticed after boiling.

Glacial acetic acid will not react and after boiling will give absolutely clear solution.

No. 2. *Differentiation of High Per cent. Ethyl Alcohol from Methyl Alcohol*.—After distilling over a few cc. of the suspected mixture to concentrate alcohol if not present as such, add one or two drops of selenic acid,  $\text{H}_2\text{SeO}_6$ , with trace of silver halogen salt (best silver bromide). Ethyl alcohol will give a white amorphous precipitate. The methyl alcohol, common wood spirit, will not give this reaction. In exceptional cases it will give crystalline precipitate, leaving solution clear. Water will dissolve the milky precipitate of the ethyl alcohol. This test can also be used for esters.

No. 3. *Differentiation of Different Alkaloids, Especially Cantharidin*.—The extracted alkaloid is dissolved in concentrated sulfuric acid, 94-5 per cent., and a trace of sodium selenite ( $\text{Na}_2\text{SeO}_3$ ) added to the solution. After heating, a purple reaction will be noticed, very characteristic, see table of color reaction of different alkaloids with same reagent.

TABLE OF COLOR REACTION OF DIFFERENT ALKALOIDS.

	$\text{H}_2\text{SO}_4$ 96%.
Digitalin <sup>1</sup> .....	Only slight coloration.
Strychnin <sup>1</sup> .....	Only slight coloration.
Brucein <sup>1</sup> .....	Rose coloration (pink).
Aconitin <sup>1</sup> .....	Only slight coloration.
Atropin <sup>1</sup> .....	Only slight coloration.
Morphin <sup>2</sup> .....	Green coloration in cold.
Codein <sup>2</sup> .....	Light brown coloration.
Caffein <sup>1</sup> .....	No coloration
Chinin <sup>1</sup> .....	No coloration in cold; in heat, slight coloration.
Spartin <sup>3</sup> .....	No coloration.
Veratrin <sup>4</sup> .....	Cherry-red coloration.
Cantharidin <sup>5</sup> .....	No coloration.

No. 4. *Test to Detect Small Amounts of Benzine in Turpentine where the Official Test did not React or Satisfy the Definite Amount Present*.—A five or ten per cent. copper sulphate solution is used (3-4 cc. for reaction):

Benzin 1 to 2 cc.	Turpentine 1 to 2 cc.
Copper sulphate, 10 per cent. sol. 3 to 4 cc., gives clear solution; to this is added a small crystal of <i>potass. iodide</i> : dissolves with purple color, when shaken turns yellowish brown after some time.	Copper sulphate, 10 per cent. sol. 3 to 4 cc.; solution is not clear; to this is added a small crystal of <i>potass. iodide</i> : purple red, which gradually fades when shaken and when pure turpentine, green coloration results.

When "rosin" besides benzine and turpentine is present, the smell can distinctly be defined; solution is of a brownish color. The amount of benzine present will make solution more or less clear.

No. 5. *Nitric Acid Test*.—The acid must be concentrated, 40 per cent., or if diluted, neutralized and evaporated to dryness, in form of a nitrate.

*Reagent*.—To two or three cc. of fuming sulfuric acid is added a trace of "powdered tellurium," an eosin red color is produced. To this fuming solution one to two cc. of 95 per cent.  $\text{H}_2\text{SO}_4$  are added. One cc. each in two test tubes is heated until decolorized. To one is added the nitrate and to the other a drop

<sup>1</sup> With  $\text{Na}_2\text{SeO}_3$ , brown coloration.

<sup>2</sup> With  $\text{Na}_2\text{SeO}_3$ , after heating, black precipitate.

<sup>3</sup> With  $\text{Na}_2\text{SeO}_3$ , no coloration.

<sup>4</sup> With  $\text{Na}_2\text{SeO}_3$ , purple coloration.

<sup>5</sup> The cantharidin as cryst. alcohol, dissolved in concentrated 96%  $\text{H}_2\text{SO}_4$  with  $\text{Na}_2\text{SeO}_3$  gives slight purple coloration in the cold. By heating, the coloration increases and gradually turns into a dark coloration. This can be changed by adding alcohol which again turns up the darker purple coloration. Cocain same as morphin.

or more of the reagent. Then both tubes are slightly heated and to the tube containing the nitrate a drop or more of the reagent is added and immediately decolorized, whereas the one without acid or nitrate is still colored eosin red. On this principle I have founded or based a quantitative test of nitric acid by titration taking a unit of 0, 1 tellurium dissolved in 10 cc. fuming acid  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$  and 10 cc. sulfuric acid, 95 per cent., added, will equal to or decolorize 0, 66 nitric acid of 66 per cent. No indicator is necessary.

*Test No. 6. Detection of Copal Amber*.—This test might not be useful, but is of the most tedious character and no book or literature will assist in this most complicated test.

The sample of the suspected mixture is finely powdered and about 4 cc. acetic ether added with 0.5 or less cobalt nitrate dissolved; then acetic acid anhydrous is added 2 cc. and about 1-2 cc. chloroform and heated. The copal mixture will dissolve, the amber mixture will not dissolve and will granulate. These two solutions added each separate to high per cent. ethyl alcohol, the copal solution will give silky color with precipitate of rosin. The amber solution will not alter the methyl alcohol solution, leaving a clear solution.

If both are together it is best to add water to the methyl alcohol solution, whereas the amber solution after shaking is still clear and the copal, if any or in small quantities, will give milky or opalescent solution.

DR. FRED. KLEIN.

## IDENTIFICATION TEST FOR CARAMEL.

The use of caramel as a coloring agent in pharmaceutical preparations, flavoring extracts, liquors and vinegar is so universal and the tests for identification of this substance having proven unsatisfactory in many instances, I submit the following reagent or solution which has been in use in our laboratory for a year with success on flavoring extracts and liquors, and, while its employment for detecting caramel in vinegar has been very limited it has given good results when put to such use.

*The Solution*.—

	Grams.
Tannic acid.....	1.00
Sulphuric acid (sp. gr. 1.84).....	0.75
Water, q. s., ad.....	50.00

Dissolve the tannic acid in about 30 cc. of water, add the sulphuric acid (the precipitate first forming will dissolve) and then the rest of the water; let stand 24 hours. Lastly, filter. This solution keeps well.

The method of using for vanilla extracts is simply to add 5 cc. to 5 cc. of the extract, heat gently until the precipitate at first formed is almost all dissolved, then, on standing for 12 hours or overnight, a light or dark brownish substance (according to the amount of caramel present) will have been precipitated. True vanilla extractive gives a very slight precipitate of a different character than that of caramel.

When whiskey, brandy or other spirituous liquors are to be examined the greater part of the alcohol is evaporated, water added and tested the same as vanilla extract.

Much time is gained by this method when working upon many samples at one time as any number of test tubes can be prepared and allowed to stand overnight, the precipitate being observed the next morning.

G. H. P. LICHTHARDT.

SACRAMENTO CITY BOARD OF HEALTH.

## TO DETERMINE FUSEL OIL IN DISTILLED LIQUORS.

The tedious and unsatisfactory methods now in use for the determination of fusel oil in distilled liquors may be replaced by the much more rapid and accurate method of Savelle with a few modifications.

To 25 cc. sample add 5 cc. of a normal alkali solution and digest for one hour on the water bath under a reflux condenser to saponify the esters, then connect with a suitable distilling apparatus and distil 25 cc.; add 5 cc. of water and distil an additional 5 cc.

To this distillate add 0.2 gram of *m*-phenylenediamine hydrochloride and boil under a reflux condenser for one hour to remove the aldehydes, after which distil, collecting 25 cc.; add 5 cc. of water and distil an additional 5 cc., bringing the distillate up to the original volume.

To this distillate add slowly an equal volume of C. P.  $\text{H}_2\text{SO}_4$  conc., heat nearly to boiling, and while still hot add 5 to 10 drops of a 1 : 1000 solution of furfural; a pink or red color will develop in the presence of the higher alcohols, which may be compared with a standard solution of amyl alcohol treated in the same manner.

By this method less than 0.01 per cent. of fusel oil can be determined and 1 part in 20,000 detected.

H. P. BASSETT.

DELAWARE EXPERIMENT STATION, NEWARK.

## BOOK REVIEWS AND NOTICES.

**Metallography.** C. H. DESCH, Graham Young Lecturer in Metallurgical Chemistry, Glasgow University. Crown 8vo. 9s. Longmans, Green & Co.

The following are the principal headings by which the book is divided into 18 chapters: Introduction, The Diagram of Thermal Equilibrium; Solid Solutions or Mixed Crystals; Ternary or More Complex Systems; Metals which are only Partially Miscible in the Liquid State; Practical Pyrometry and Thermal Analysis; The Preparation of Microsections; The Microscopical Examination of Prepared Sections; The Crystallization of Metals and Alloys; Undercooling and the Metastable State; Diffusion in the Solid State; The Physical Properties of Alloys; Density, Thermal Expansibility, Hardness, Electrical Conductivity, Thermo-electric Power, Magnetic Properties; Electromotive Force and Corrosion; The Construction of the Equilibrium Diagram; Molecular Condition of Metals in Alloys and the Nature of Inter-metallic Compounds; The Plastic Deformation of Metals and Alloys; The Metallography of Iron and Steel; The Metallography of Industrial Alloys.

Metallography is defined as a study of the internal structure of metals and alloys and of its relation to their composition and to their physical and mechanical properties. The book, which is one of the text-books of physical chemistry edited by Sir William Ramsay, follows this line and summarizes our present knowledge in a very clear and logical way.

Taking the diagram of thermal equilibrium and the freezing point curve for a beginning, the different type cases are developed step by step. The Phase rule is given in brief and its application to alloys is shown, while the section on the ternary systems is well written. The chapter on the crystallization of metals and alloys is very clear indeed and the illustrations well chosen.

The latter part of the book, dealing with the Metallography of Iron and Steel, gives us a good summary of our present knowledge and includes Upton's diagram. An appendix shows in tabular form the systems of which the equilibrium diagrams have been published, with the probable formulae of intermetallic compounds formed.

Mr. Desch has written an excellent book in a convincing way which will be welcomed alike by the student and the practical man. A possible criticism is that the section on practical pyrometry and thermal analysis is too condensed for the general reader, but the references given will help the student over any difficulty. In conclusion, the author is to be congratulated

in setting forth so important a subject as metallography in so instructive and so interesting a manner.

W. CAMPBELL.

**Transactions of American Institute of Chemical Engineers.** Vol. 2, 1909. Cloth, large 8vo. pp. 308. New York: Published by the Institute. For sale by D. Van Nostrand Co.

The second volume of the transactions of the American Institute of Chemical Engineers contains a number of valuable and readable articles, in addition to the official transactions, the constitution and a list of officers, committees and members. The papers are nineteen in number and are written by well-known chemical engineers, among whom are the names of Prof. Chas. E. Munroe, Samuel P. Sadtler, Wm. M. Booth, A. C. Langmuir and Edw. R. Taylor. The Institute has grown so that it now consists of about 130 members. The volume will find a wider circle of readers than its own members, as it will be found of interest to many chemists and engineers. Of the papers the following are selected to show the general character of the volume:

Chemical Industries of America, Chas. E. Munroe; Conservation and the Chemical Engineer, Samuel P. Sadtler; Efficiency Limits in the Power-Gas Producer, Prof. Wm. D. Ennis; Heat Efficiency of Smokeless Combustion and Heat-Absorbing Capacity of Boilers, A. Bement; Creosote Oil from Water Gas Tar, Samuel P. Sadtler; A Method of Clay Control for Manufacture of Cement, John G. Dean; The Utilization of Waste India Rubber, Stephen P. Sharples; Commercial Extraction of Grease and Oils, Wm. M. Booth; Glycerine Refining in Multiple Effect Stills, F. J. Wood; Electric Furnace for the Smelting of Iron Ore, Edward R. Taylor.

**Allen's Commercial Organic Analysis.** Vol. II. Oils and Fats.

Edited by HENRY LEFFMANN and W. A. DAVIS, with the co-operation of C. AINSWORTH MITCHELL, LEONARD ARCHBUTT, C. REVIS, E. R. BOLTON, C. A. KLEIN, W. ROBERTSON, JOHN ADDYMAN GARDNER and AUGUSTUS H. GILL. Large 8vo. pp. 520. Philadelphia: P. Blakiston's Son & Co. 1910. Price, \$5.00 net.

Following the new plan in the present edition of Allen's widely known "Commercial Organic Analysis," the editors have produced what is to a large extent a new work. The best distinctive feature of the previous editions, namely, the general descriptive matter, is prominent in the fourth edition. It is larger than the third edition by 133 pages, but this numerical difference scarcely covers the extension of matter. C. Ainsworth Mitchell has contributed the chapter on General Properties and Analytical Methods; Leonard Archbutt, Special Characters and Methods; Butter Fat is treated by Cecil Revis and E. R. Bolton; Lard, by C. Ainsworth Mitchell; Linseed Oil, by C. A. Klein; Higher Fatty Acids, by W. Robinson; Soap, by Henry Leffmann; Glycerol, by W. A. Davis; Cholesterols, by John A. Gardner; and Wool-Fat and Cloth Oils, by Augustus H. Gill. The book is essentially a descriptive and analytical work. It enters into technology only to the extent necessary to make the analytical control methods intelligible. More concise than the works of Lewkowitsch, Hefter, Benedikt Ulzer and Ubbelohde, it is generally accurate, painstaking and well up-to-date.

**Theorie der Gewinnung und Trennung der Aetherischen Oele durch Distillation.** By DR. C. VON RECHENBERG. Large 8vo. pp. v + 490. Miltitz: Schimmel & Co.

The present work is an excellent addition to the literature of the volatile oils. Previously the student was limited in the study of the subject to the treatment of moderate length only in Gildmeister & Hoffmann's "Volatile Oils." The first chapter takes up the practice of distillation, beginning with a general

description of the processes and apparatus as applied to the distillation of volatile oils. Next in order in the same chapter is a brief account of the occurrence of volatile oils in plants, illustrated with histological cuts of the oil-bearing parts of plants. Then follows a description of the preparation of plants for distillation, together with an account of the losses which may occur and the general methods of distillation. The details of present-day practice and the forms of stills used are given. The second chapter takes up Dalton's law of diffusion; the third, distillation of mixtures of insoluble fluids; the fourth, distillation under increased and diminished pressure; the fifth, distillation with superheated steam; sixth, physico-chemical phenomena in plant distillation. Thus the second, third, fourth, fifth and sixth chapters are largely theoretical. In the seventh chapter a description is given of the practice in various parts of the world, of distilling essential oils on the small scale. This chapter is of a descriptive nature, is well illustrated and of general interest. The eighth chapter considers molecular association and dissociation and their influence on vaporization. The ninth chapter takes up boiling points and vapor tensions of substances, and includes a table of the boiling points under various pressures of many organic substances, a number of which occur in the volatile oils. This chapter concludes with an excellent bibliography of the works used in the preparation of the table. The tenth chapter considers solution in general; the eleventh, distillation of mixtures of substances of limited solubility; the twelfth, distillation of homogeneous mixtures with minor boiling temperatures; the thirteenth, distillation of homogeneous mixtures without constant boiling point; the fourteenth, distillation of homogeneous mixtures with major boiling temperatures. It is stated by the author that the work will form a part of the second edition of Gildemeister & Hoffmann's "Die ätherischen Öle," and pages are numbered from 259 to 751 as though reprinted from another work. It appears that the work could be somewhat better arranged, by bringing together all of the theoretical parts in one place, and the practical portions in another. Such an arrangement would make it somewhat more systematic. In general, it is to be commended as an excellent addition to the literature.

**Technologie der Fette und Öle.** By GUSTAV HEFTER, with co-operation of O. HELLER, G. LUTZ, FELIX KASSLER, and others. Vol. III. Large 8vo. pp. xii + 1022. Well illustrated. Berlin: Julius Springer. 1910. Price, paper 32 Marks; bound 35 Marks.

With the third volume of this valuable work out of the press, chemists in the oil and fat industries may look for its speedy completion. The two preceding volumes gave promise that the work as a whole would be in all probability the most comprehensive reference work on the subject of fats and oils industries which has yet been published, and the third volume reaches the high standard set by the first two volumes. The arrangement of the subject matter is as follows: Edible Oils and Fats; Plant and Animal Lubricating Oils and Fats; Polymerized Oils; Oxidized Oils; Sulphurized Oils; Iodized, Brominated, and Nitrated Fats; Textile Oils; Stearic Acid Manufacture; Candle Manufacture. Prof. Max Bottler, Würzburg, has contributed the chapter on burning oils and Dr. Herbig, of Chemnitz, the chapter on textile oils. While all portions of the volume are commendable, those divisions devoted to edible oils and fats, stearic acid and candle manufacture are especially good for their excellent arrangement and classification and comprehensive treatment. If any criticism can be brought against the chapter on edible oils and fats, it would be the failure to give due prominence to the ever-increasing use of tropical vegetable oils and fats in the manufacture of oleomargarine. In the chapter on stearic acid manufacture, following an excellent general and historical introduction,

the methods of saponification by means of the autoclave, sulphuric acid, Twitchell's process, and the enzymes are given proper consideration. The treatment of waste fats and glycerine is reserved for Volume IV. It is needless to add that, inasmuch as the work issues from the press of Julius Springer, the typography, paper and make-up are the best.

**The Polytechnic Engineer.** Vol. X. Large 8vo. pp. 144. Brooklyn: Published by the Undergraduates of Polytechnic Institute of Brooklyn. 1910.

Volume X of the *Polytechnic Engineer* contains four excellent articles of special interest to chemists and chemical engineers. They have the following titles and authors: The Investigation of Congo Blue and Preparation of Congo White, by Irving W. Fay, A. H. Tag and M. G. Hawkins; Some Experiments on the Case-Hardening of Steel by Gases, John C. Olson, John R. Briery, and John S. Weiffenback; Initial Temperatures at which Oxides of Metals Give up Oxygen to Reducing Gases, by Irving W. Fay, Albert F. Seeker, Frederick H. Lane and Geo. E. Ferguson; A Liquid which will Dissolve Cotton, by Irving W. Fay and Chas. H. Lewis. The volume as a whole is commendable and is well printed.

**Engineering Chemistry.** Fourth Edition. By THOMAS B. STILLMAN. 8vo. pp. ix + 744. Easton, Pa.: Chemical Pub. Co. 1910. Price, \$5.00.

The three previous editions of Dr. Stillman's work have proved of the greatest usefulness to chemists in works laboratories. The reason for this is that they have contained a large amount of specific information concerning the physical and chemical examination of gas, water, materials of construction and engineering materials not readily accessible elsewhere. The work is so widely known and has been so favorably received in the past that special comment would be superfluous. In the present edition the subject of pyrometry is handled by Edw. A. Uehling and W. H. Bristol. "Foundry Chemistry" is treated by Herbert E. Fields, "Acetylene" by R. E. Bruckner. The official methods of sampling iron ore as adopted by the U. S. Steel Corporation are included. Many other additions have been made in the present edition in bringing it down to date. It is a useful book for all works laboratories and colleges.

The North Carolina Geological and Economy Survey has issued Bulletin No. 18, **Bibliography of North Carolina Geology, Mineralogy and Geography**, with list of maps, by FRANCIS BAKER LANEY and KATHERINE HILL WOOD; and Bulletin 21, **Gold Hill Mining District of North Carolina**, by FRANCIS BAKER LANEY.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### ANNOUNCEMENT OF THE TWENTY-SEVENTH ANNUAL CONVENTION, ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, NOVEMBER 10-12, 1909.

The twenty-seventh convention of the Association of Official Agricultural Chemists will be held in Washington, D. C., at the Raleigh Hotel, corner of Twelfth Street and Pennsylvania Avenue, opening on November 10th, at 9 o'clock.

The hotel rates will be as follows, European plan:

Room for one person.....	\$2.00
Double room for two persons.....	3.00
Room and bath for one person.....	3.50
Double room and bath for two persons.....	5.00

As the hotel will provide a large hall on the top floor of the building for the convention, as well as other facilities for the meeting, it is urged that the members make the Raleigh their headquarters, if possible, and reserve their rooms a few days in advance.



## ORDER OF BUSINESS.

Thursday, November 10th.

Morning session: Phosphoric acid; Nitrogen; Potash; Soils; Inorganic plant constituents.

Afternoon session: Appointment of committees (resolutions, etc.); Insecticides; Water; Committee A on recommendations of referee; Report of special committees—(amendments to constitution; appropriation; availability of phosphoric acid; compilation of by-laws; food standards; unification of terms; standardization of alcohol tables; testing of chemical reagents; unification of methods of analysis of fats and oils).

Friday, November 11th.

Morning session: Food adulteration (reports to be called for in order given in list of associate referees).

President's address (special order for 12 o'clock).

Afternoon session: Food adulteration continued. Separation of nitrogenous bodies (meat proteids; milk and cheese proteids; vegetable proteids). Committee C on recommendations of referees.

Saturday, November 12th.

Morning session: Dairy products. Foods and feeding stuffs. Sugar (chemical methods and molasses methods). Committee B on recommendations of referees. Committees (resolutions, constitution, etc.). Tannin.

Afternoon session: Drugs and medicinal plants.

*Referees Please Note.*—Recommendations in triplicate, together with an abstract of the report, should be in the hands of the respective chairmen of committees A, B, and C, by October 17th at the latest, if action is to be taken at the meeting and the necessary approval of the Committee on Revision as a whole obtained (see pages 168 and 205 of Bulletin 132, Bureau of Chemistry, or Circular 52, pages 19 and 32).

H. W. WILEY,  
Chief, Bureau of Chemistry,  
Secretary, Association of Official  
Agricultural Chemists.

WASHINGTON, D. C., August 13, 1910.

## AMERICAN ELECTROCHEMICAL SOCIETY.

The Eighteenth General Meeting of the American Electrochemical Society will be held in Chicago, October 13th to 15th, by invitation of the newly formed Chicago Section. The program will include excursions to the Illinois Steel Co.'s plant at South Chicago, the Indiana Steel Co.'s plant at Gary, the U. S. Smelting, Refining and Mining Co.'s plant at Grasselli, the packing plants, etc. Dr. H. N. McCoy, of the University of Chicago, is chairman of the Committee on Arrangements.

**EINLADUNG ZUR 26. JAHRESVERSAMMLUNG DES  
DEUTSCH-AMERIKANISCHEN TECHNIKER-VER-  
BANDES. ABZUHALTEN VOM 1. BIS 5. SEP-  
TEMBER D. J. IN NEWARK, N. J.  
HAUPTQUARTIER: L. ACHTEL-  
STETTER, 842 BROAD ST.**

## FESTORDNUNG.

DONNERSTAG, DEN 1. SEPTEMBER.

Vormittags 10 Uhr: Sitzung der Delegaten im Hauptquartier.

Nachmittags 8 Uhr: Empfang und Begrüssung der Gäste im Hauptquartier auf Einladung des T. V. Newark.

FREITAG, DEN 2. SEPTEMBER.

Vormittags 9 Uhr: Zusammenkunft im Hauptquartier. Von da Abfahrt mit der Strassenbahn (Orange-Linie) nach

Edison's Laboratorien, West Orange, N. J. Von New York nehme man die Erie-Bahn bis West Orange, ab "Chambers Street Ferry," punkt 9 Uhr morgens. Vom Bahnhof West Orange etwa 8 Minuten zu Fuss nach den Laboratorien.

Vormittags 10-11 Uhr: Beginn der Besichtigung der Werke.  
Nachmittags 1 Uhr: Gemeinschaftliches Gabelfrühstück im Hauptquartier.

Nachmittags 2-3 Uhr: Abfahrt vom Hauptquartier mit der Strassenbahn (Turnpike- oder Kearny-Linie) nach Henry R. Worthington Hydraulic Works, Harrison, N. J.

Nachmittags 3 Uhr: Beginn der Besichtigung der Werke.

Nachmittags 8 Uhr: Festkommers im Hauptquartier.

## Tagesplan für die Damen.

Zum Vormittags-Ausflug sind die Damen freundlichst eingeladen.

Nachmittags 3 Uhr: Abfahrt vom Hauptquartier mit der Strassenbahn nach Krügers "Greisenheim." Dort Preiskegeln und

Nachmittags 6 Uhr: Gemeinsames Abendessen auf Einladung der Damen des T. V. Newark.

Hierauf Besuch des Sommertheaters im "Olympic Park".

SAMSTAG, DEN 3. SEPTEMBER.

## Familienausflug.

Vormittags 10 Uhr: Zusammenkunft im Hauptquartier.

Vormittags 10-11 Uhr: Abfahrt in Sonderwagen der Strassenbahn (Orange-Linie bis Endpunkt), Spaziergang über "Eagle Rock" nach "Crystal Lake Park Hotel" (30 Minuten zu Fuss, auch Omnibusverbindung).

Nachmittags 1 Uhr: Gemeinschaftliches Mittagessen.

Danach Unterhaltungen im Freien: Gesellschaftsspiele, Bootfahren u. s. w. Photographische Aufnahme aller Festteilnehmer.

Bei ungünstiger Witterung steht ein grosser Tanzsaal zur Verfügung.

SONNTAG, DEN 4. SEPTEMBER.

Vormittags 10 Uhr: Allgemeiner Technikertag im Hauptquartier Berichte der Delegaten und Jahresberichte. Nachher Frührschoppen.

Nachmittags 1 Uhr: Gemeinschaftliches Gabelfrühstück.

Nachmittags 3 Uhr: Vortrag von Herrn Dr. L. H. Friedburg, Professor am "College of the City of New York," Ehrenmitglied des T. V. Brooklyn.

"Radioaktivität und Beständigkeit der Elemente mit Seitenlicht auf Transmutation und Alchemie."

Nachmittags 8 Uhr: Festessen und Ball im Hauptquartier.

MONTAG, DEN 5. SEPTEMBER.

(Labor Day.)

Vormittags 11 Uhr: Katerfrühstück und Abschied.

Nachmittags: Unoffizieller Ausflug nach Coney Island nach Verabredung.

Absteigequartier: Continental Hotel, 454 Broad St., Newark, N. J.

## Der Fest-ausschuss:

Z. Freund, Obmann.	H. Hoppe, Schriftführer.	
Th. Koch, Rechnungsführer.		
B. A. von Bergen,	Kurt Ledig,	Phil. Volz,
Wilh. Heck,	L. F. Mergott,	E. W. Zeh,
	S. I. Oesterreicher.	

## Der Ausschuss der Damenvereinigung:

Frau E. F. Harder,	Frl. E. Koch,	Frau Th. Teimer,
Frau Wilh. Heck,	Frau S. I. Oesterreicher,	Frau A. Wack,
Frau Th. Koch,	Frau J. H. Sebald,	Frau E. W. Zeh,
	Frl. H. Sebald.	

## Delegaten:

Verein.  
Baltimore,  
Brooklyn,  
Chicago,  
Newark,  
New York,  
Philadelphia,  
Pittsburg,  
Rochester,  
Washington,  
Dr. H. C. P. Weber,

Delegat.  
Emil Eiselt,  
Hermann Dann,  
A. Sonderhof,  
Georg Sulzer,  
Wm. Mueser,  
O. Gussfeldt,  
H. Schütte,  
O. Kallenbach,

Stellvertreter.  
Heinrich Turk.  
August Wittel.  
B. A. von Bergen.  
H. J. Schäfer.  
C. D. Rinald.  
A. C. Sprecht.  
Arno Greiner.  
Dr. S. O. Graser.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

963,174. Process for Making Concentrated Sulfuric Acid. OTTO PROLSS, of Kansas City, Missouri. July 5, 1910.

This is a process in which sulfuric acid of a strength of 66° is produced by independently denitrating and concentrating different bodies of liquor, using sulfurous acid as gas in this connection, and thereafter bringing together the hot gases from the concentrating means, and the cooler gases from the denitrating means, and subjecting them to the action of the weak sulfuric acid.

In carrying out the process there are used three independent and separate chambers, which may be within one or more structures or buildings, but which, as shown in the accompanying illustration, are in three towers,  $A^1$ ,  $A^2$  and  $B$ , each of which may be a Glover tower of ordinary construction.

With the lower end of each of the towers  $A^1$ ,  $A^2$  communicates a pipe or flue  $E$ , from which hot sulfurous acid gas is conducted to the tower from the burners, or roasting furnaces, etc., and from the top of each tower  $A^1$ ,  $A^2$  a pipe or flue  $V$  extends laterally to the tower  $B$ . From the tower  $B$  a pipe or flue, 4, extends to an exhauster,  $F$ , of any suitable character to convey the gases to the chambers; and suitable coolers,  $C^1$ ,  $C^2$ ,  $C^3$ , are arranged to receive the liquor from the bottom of each of the towers.

The tanks  $T^1$ ,  $T^2$  and  $T^3$ , are suitably connected with the towers  $A^1$ ,  $A^2$ , and  $B$  respectively, by means of suitable dis-

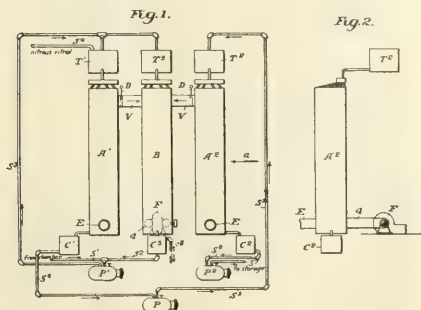
tributing devices. The liquor in  $C^3$  contains nitrogen oxides in solution. The weak acid from tank  $T^3$  passes down the tower  $B$  and is delivered into the cooler  $C^3$ , an overflow pipe,  $S^8$ , being provided which may lead to a storage tank or the chambers. A pipe,  $S^9$ , supplies the tank  $T^1$  with nitrous vitriol from the Gay-Lussac tower. The liquor from tank  $T^1$  passes down the tower  $A^1$ , collects in the cooler  $C^1$ , and is delivered by means of a pipe,  $S^4$ , to the pump  $P$ , which delivers the liquor by means of a discharge pipe,  $S^5$ , to the tank  $T^2$ . The liquor from the tank  $T^2$  passes down the tower  $A^2$ , discharges into the cooler  $C^2$ , which delivers by a pipe,  $S^6$ , to a pump,  $P^2$ , which is connected to a discharge pipe,  $S^7$ , leading to the storage tank.

The hot gases from the tower  $A^2$  pass to tower  $B$  and the cooler gases from the tower  $A^1$  also pass to the tower  $B$ , suitable dampers,  $D$ ,  $D$ , regulating the flow of these gases, and as these are mixed together in the tower  $B$ , they are subjected to the action of weak sulfuric acid, which is discharged into the tower  $B$  from the tank  $T^3$  supplied from the lead chambers and from tank  $C^3$  through  $S^3$  as described and properly distributed in the tower.

In operating the apparatus both towers are supplied through the flues  $E$  with the sulfurous acid gas, and the tower  $A^1$  is fed with a mixture of chamber acid and nitrous vitriol, as usual, with the result that the liquor at the bottom of the tower and carried to the cooler  $C^1$  is of a strength of from 60° to 62° Bé. This liquor is then elevated to the top of the tower  $A^2$  by the pump  $P$ , the apparatus being so regulated that a concentration will be effected in the tower  $A^2$  and will in all cases produce a liquor exceeding 60° Bé., and in order to obtain this liquor free from nitrogen oxides, no niter in any shape must be admitted to the tower  $A^2$  so that the denitrating is effected wholly in the other tower. Owing to the high concentration of the acid in the tower  $A^2$  the gases issuing therefrom through the pipe  $V$  are very hot and must be cooled down before they enter the lead chambers.

The gases issuing from the denitrating tower, of moderate temperature and laden with nitrogen compounds, and those issuing from the concentrating tower, and free from nitrogen compounds and of high temperature, are brought together in the intermediate tower, the function of which is to unite and thoroughly mix these gases and reduce the temperature of the gases from the concentrating tower so that the mixed gases are at a temperature which will not be injurious in the further operations. To this end these mixed gases are subjected in the intermediate tower to the action of the cool, weak sulfuric acid, the operation being so regulated that the gases will issue from the intermediate tower at such temperature as is demanded by mechanical and chemical considerations. In other words, my process splits the available burner gas into two parts: one part is used to denitrate the nitrous vitriol and concentrate the weak sulfuric acid formed in the chambers, and the other part of the burner gases is used to effect a further concentration of the 60–62° sulfuric acid thus produced. The waste gases resulting from the two parallel operations are then brought together, mixed and cooled in a subsequently intermediate tower before being admitted to a series of chambers and Gay-Lussac towers.

The liquor from the intermediate tower is suitably cooled in the cooler  $C^3$  and constitutes part of the body of liquor which is operated upon in denitrating and concentrating in the tower  $A^1$ . The liquor from the tank  $C^2$  is carried by a pump,  $P^2$ , to a suitable storage reservoir. By means of this process sulfuric acid containing as high as 96° ( $H_2SO_4$ ) has, it is claimed, been obtained without any greater amount of fuel, labor or supervising than is ordinarily required in producing acid of much lower strength, and by means of properly constructed flues and dust chambers the acid may be had of the proper light color, or freedom from color.

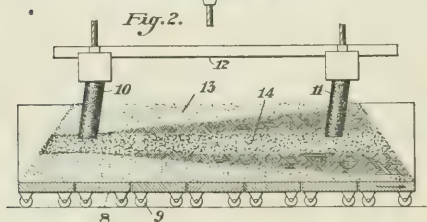
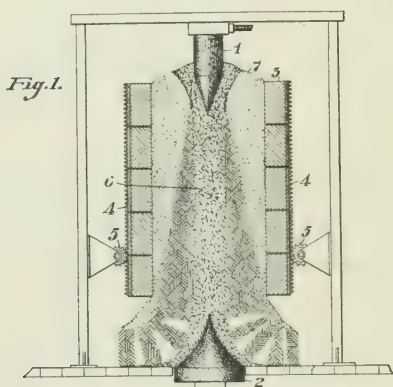


tributing devices. A pump,  $P^1$ , supplied by a pipe,  $S^1$ , with chamber acid from the chambers, and by a pipe,  $S^2$ , from the cooler  $C^3$ , delivers the liquor through the discharge pipe  $S^3$ , and branch pipes into the tanks  $T^1$  and  $T^2$ . It will be noted

965,142. Method of Making Silicon Carbide. FRANK J. TONE, Niagara Falls, New York. July 19, 1910.

This invention relates to the production of silicon carbide, and is designed to reduce the number of furnaces necessary for a certain output and increase the output of single furnaces.

Under the present practice, a stationary electric furnace is employed consisting of a long rectangular receptacle with stationary electrodes at opposite ends, the charge of coke and sand being placed around a resistance core embedded therein. The current passes through the resistance core which is in contact with the electrodes in its end portion. The furnace is operated for a certain period varying from twenty-four to



thirty-six hours, after which the current is cut off, the furnace cooled down and the contents removed. It is then recharged and the operation repeated. The period of cooling and recharging occupies several days, and consequently, a series of furnaces is necessary in order to keep one furnace in operation at all times. The output of a furnace is therefore comparatively small.

This invention is designed to afford a continuous process in which there is no cooling down or cessation of operation, the current being continuously supplied as are also the charge and core. The finished products are also removed in a substantially continuous manner.

The accompanying illustration shows a furnace of vertical type in which the process may be carried out. The side walls of the furnace are formed of transversely divided refractory sections, 3, secured to or having rack sections, 4, engaging with pinions, 5, which may be operated to give a continuous or intermittent downward movement to the wall sections. The wall sections may be guided within any suitable supports or guides to hold the charge and core in place and are added at the top and removed at the bottom in the downward movement.

The resistance conductor consists of granular core material, 6, which is supplied at and around the upper electrode, and is

surrounded by the charge mixture of carbon and silicious material, 7, which is also supplied at the top. As the containing walls move downward, they carry with them the charge and resistance core. The rate of motion is so regulated that when the charge shall have reached the lower electrode, it will have been converted into silicon carbide, the zone of carbide which is formed being of such diameter as will represent an economical rate of production. The lower electrode is preferably pointed or conical in shape, so that the core material and finished product will be given an outward movement, and fed into a position where it may be readily removed from the furnace.

964,268. Apparatus for Smelting Ores Yielding a Volatile Metal. WOOLSEY MCA. JOHNSON, of Hartford, Conn. July 12, 1910.

This apparatus comprises an electric smelting furnace, a reducer for the volatile reaction products therefrom, and a condenser.

The furnace is so constructed as to facilitate the production and removal of the fluid slag, and the reducer comprises a chamber for containing a body of coke, coal or other carbonaceous material, provided with electrodes in contact with said body.

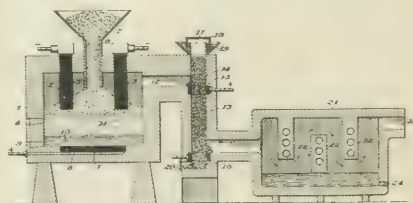
In the accompanying illustration the furnace is shown as comprising a smelting chamber, 2, formed of or interiorly lined with a suitable refractory material, 3, 3, representing carbon electrodes supported in the upper part of the furnace and terminating above the level of a slag tap, 4. The electrodes 3, 3 are of the same polarity, the opposing electrode 5 being embedded in the hearth of the furnace, in electrical contact with a conductive plate or bar, 6. 7 is a hopper for the introduction of the charge 8, and 9 is a tap for the removal of non-volatile metals or matte, 10.

The volatile reaction products pass through the outlet 12 and thence through a column, 13, of coke or coal contained in a chamber, 14, and adapted to be heated by an electric current passing between upper and lower ring electrodes, 15, 16, set in the walls of the reducing chamber. The reducing chamber is preferably connected electrically in series with the furnace.

From the reducing chamber 14 the vapors, free from carbon dioxide, aqueous vapor and other compounds capable of oxidizing zinc, pass to a suitable condenser, 21, shown as provided with water-cooled partial partitions, 22, constructed to direct the vapors in a tortuous path.

23 is the outlet for non-condensing gases, and 24 the metal tap.

In the use of this apparatus there is incorporated with the charge only such proportion of carbon as is necessary for the



reduction of the metallic constituents thereof, producing thereby an easily fusible slag which may be tapped off as desired; any lead, copper or iron accumulates in metallic state beneath the slag and is withdrawn as desired, and fresh portions of the charge may be admitted continuously or at intervals.

This invention consigned to the Continuous Zinc Furnace Company, of Hartford, Connecticut.



964,901. Process of Treating Combustible Gas. HENRY L. DOHERTY, of New York, N. Y. July 19, 1910.

This invention consists of a method of treating combustible gases (such as blast-furnace gases and what is known as Mond gas) containing an appreciable amount of carbon dioxide by preheating the gas to a temperature sufficient to supply the heat required for the dissociation of the carbon dioxide—or to a temperature as near to such temperature as is practicable—and then passing the preheated gas through the fuel bed of a down-draft producer, whereby the contained carbon dioxide is reduced to carbon monoxide with the production of a gas nearly free from carbon dioxide and which is particularly suitable for use in gas engine and high temperature work.

The object of the invention is to furnish a process for carrying out such treatment of the gas without the addition thereto of a

Mond gas leaving the recuperator then passes to the ordinary scrubbing towers 17, 18 and 19, where the ammonia is removed from the gas. These towers do not necessarily differ from the ones at present in use. From 19 the gas is withdrawn by the exhauster 20 and forced through the pipe 21 to the recuperator 22. This recuperator is in reality two separate recuperators, one for air and the other for gas, built, side by side, within the same shell. The section shown in Fig. 1 is through one of the gas flues, but the construction is identical on the air side.

The cold Mond gas and air passing through the recuperator go next to their respective superheaters, 30 and 31. These are built within the same shell but are so arranged that there is no communication between the gas and air sides.

The process is defined in the inventor's patent as consisting in treating a combustible gas containing carbon dioxide which consists in removing from said gas substantially all of its condensable water-vapor, superheating the major portion of said gas in a suitable superheater, and passing the superheated gas downward through a deep bed of fuel in a suitable enclosed chamber, said high temperature to reduce the carbon dioxide of said gas by adding to said gas, previous to passing the same through said fuel bed, the minimum quantity of oxygen that will maintain said fuel bed at the desired temperature.

The accompanying illustration shows the apparatus in which the process is carried out.

965,714. Process for Extracting or Separating Precious Values from Ores. JAMES S. ISLAND, Toronto, Ontario, Canada. July 26, 1910.

This invention relates to a process of extracting the precious values from ores, by reducing the mineral ores to a soluble state or salts, by subjecting the ore to a mixture of sulfuric and hydrochloric acids.

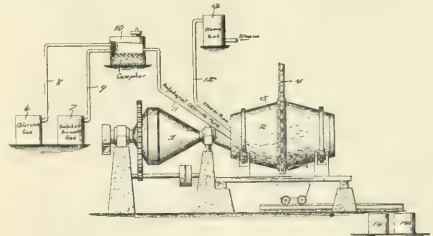
The ore, if coarse, is crushed by a suitable crusher (not shown) and then pulverized by a pulverizer. The ore is pulverized to a grade, that will pass through a hundred mesh screen, then deposited in a converter or separator, where it is subjected to the

large volume of inert nitrogen such as is unavoidably introduced into the gas in the method of carrying out such treatment heretofore known.

The method of operation is as follows:

Air enters the bottom flues of the recuperator 4 through the dampers 1, 2 and 3 which regulate the volume and distribution of the air passing into the recuperator. Passing through the air flues of 4 the air comes into contact with a layer of water which is maintained in the necessary number of flues to insure proper saturation of the air current. The hot gas from the producer passes through the gas flues enveloping the air flues its direction of flow being parallel to, but opposite in direction to the air current. The greater part of the sensible heat which the gas carries out of the producer is thus returned to the latter in the heated air and water vapor. The hot air-water vapor current after leaving the recuperator is introduced into the lower part of the gas producer 6, through the pipe 5. Passing upward through the fuel bed in producer 6, the oxygen and part of the water of the air current react with the fuel therein and form "Mond" gas in the ordinary manner. This gas passes off from the producer 6 through the pipe 7 and thence through the gas flues of the recuperator 4.

In order to maintain as high a temperature differential, as possible, between the air current and gas current it is desirable to secure the evaporation of the water as low down in the recuperator as possible. For this reason, I introduce the water to the air flues at such a point that the air passing through the flues is loaded with proper quantity of water. All the water evaporated in each flue is, preferably, run into the uppermost water pan in use and the pans below supplied by the overflow from this. Dams in the flues having water connections insure the maintenance of a shallow layer of water in the flues and thus form water pans of the bottom of the sections. If the amount of evaporation is lower than is required, water is admitted to a section higher up in the recuperator. The cooled



sulfuric and hydrochloric acids. These sulfuric and hydrochloric acids are produced by passing a mixture of chlorine and sulfur dioxide gases over an area of camphor, then together with the steam, is projected into the converter separator, thereby producing sulfuric and hydrochloric acids.

When the sulfuric and hydrochloric acids come in contact with the ore in the converter or receptacle, it reduces the ore and the metal therein, into a soluble salt.

The process is defined in the patent as consisting in separating the metal values from ores, by reducing or converting the metal values into soluble salts, by subjecting the ores to a chemical fluid, composed of chlorine, sulfur dioxide and camphor, then combining this fluid with steam, thereby producing sulfuric and hydrochloric acids.

The accompanying illustration shows the apparatus in which the process is carried out.

## OFFICIAL REGULATIONS AND RULINGS.

## FOOD INSPECTION DECISION NO. 122.

*The Labeling of Port and Sherry Wines Produced in the United States.*

A hearing was held on March 21, 1910, before the Secretary of Agriculture and the Board of Food and Drug Inspection on the labeling of wines produced in California, which for many years have been known as "California Port" and "California Sherry," respectively.

It is the view of the Department that the terms "Port" and "Sherry" without qualification are properly applied only to the products from Portugal and Spain, respectively, but it is held that domestic ports and sheries are not misbranded if the terms "Port" or "Sherry," as the case may be, are qualified by the name of the State where the wine is produced.

F. L. DUNLAP,  
GEO. P. McCABE,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., May 31, 1910.

## FOOD INSPECTION DECISION NO. 123.

*Labeling of Rices.*

Inquiries have been received as to what is the proper branding under the food and drugs act of certain varieties of rice which have come to be known under geographic names. It is well known among the trade that there are current in commerce in the United States varieties of rice grown in Japan and varieties of rice grown within the United States from seed originating in Japan, which are marked and sold as "Japan Rice," irrespective of origin, and that a variety of rice grown in Mexico is imported as "Honduras Rice." The names "Japan Rice" and "Honduras Rice," used without qualification, in the opinion of the Board, clearly convey the impression to consumers that the rices are grown in Japan and Honduras, respectively, and if applied to rices not there grown, constitute misbranding within the meaning of Section 8 of the foods and drugs act, which provides:

That the term "misbranded" as used herein shall apply \* \* \* to any food or drug product which is falsely branded as to the State, Territory, or country in which it is manufactured or produced.

The labeling of rices, which have come to be known under geographical names, and which are not grown in the State or country which the names indicate, is covered by Regulation 19, paragraph (c), reading as follows:

The use of a geographical name in connection with a food or drug product will not be deemed a misbranding when by reason of long usage it has come to represent a generic term and is used to indicate a style, type, or brand; but in all such cases the State or Territory where any such article is manufactured or produced shall be stated upon the principal label.

To meet the requirements of this regulation rices grown within the United States, labeled "Japan Rice," should have also plainly stated on the label "Grown in the United States;" rices grown in Mexico or Louisiana, for example, labeled "Honduras Rice," should have also stated plainly on the label "Grown in Mexico," or "Grown in Louisiana," as the case may be.

There are also on the market varieties of rice labeled "Carolina White" and "Carolina Gold," which are grown in North and South Carolina, and also in any other States from Carolina seed. The Board is of the opinion that the names "Carolina White" and "Carolina Gold" by long usage have come to mean

particular varieties of rice rather than rice grown in North or South Carolina, and such rices will not be held to be misbranded if plainly labeled "Carolina White" or "Carolina Gold," as the case may be, whether qualified or not, as growers or packers may see fit, by a statement of the name of the locality where the rice is actually grown. On the other hand, if it is desired to designate rices grown from Carolina seed in States other than North and South Carolina as "Carolina Rice," there should also be plainly stated on the label the name of the locality where the rice is actually grown, as, for example, "Carolina Rice, Grown in Arkansas."

H. W. WILEY,  
F. L. DUNLAP,  
GEO. P. McCABE,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., June 16, 1910.

## FOOD INSPECTION DECISION NO. 124.

*Labeling of Stock Feed.*

It has been brought to the attention of the Board of Food and Drug Inspection that considerable uncertainty exists in the minds of manufacturers of stock feed as to what ingredients are included within the terms "nitrogen-free extract," "carbohydrates," and "sugar and starch." Confusion in this particular results in part from the varied interpretation given to the feeding stuff laws of different States. Each of the terms has a definite significance. The term "nitrogen-free extract" includes starch, sucrose, reducing sugars, pentosans, organic acids, coloring matter, and certain other ingredients in small quantities, and the amount of nitrogen-free extract present in a stock feed is determined by subtracting the sum of the moisture, crude fiber, protein, fat, and ash content from 100 per cent. Stock feed will not be held to be misbranded on account of statements on labels of the "nitrogen-free extract" content if analysis shows that the amount obtained by this method is correctly declared.

The term "carbohydrates" includes most of the specified ingredients which make up the nitrogen-free extract, plus crude fiber, but does not include organic acids and coloring matter. The amount of ingredients included in nitrogen-free extract which are not carbohydrates is so small in stock feeds that they may be disregarded in stating the amount of carbohydrates, and stock feeds will not be held to be misbranded on account of statements on labels of the proportion of carbohydrates if analysis shows that the percentage of carbohydrates declared equals the percentage of nitrogen-free extract obtained as indicated, plus the percentage of crude fiber.

Sugar and starch are carbohydrates and are included in determining the amount of carbohydrates present in stock feed. The term "starch and sugar," however, is properly applied only to the actual starch, sucrose, and reducing sugars contained therein, and stock feed will not be held to be misbranded on account of statements on labels of the percentage of starch and sugar, as such, if the percentage stated is the correct percentage of the amount of the starch, sucrose, and reducing sugars actually present.

This decision will go into effect January 1, 1911.

H. W. WILEY,  
GEO. P. McCABE,  
F. L. DUNLAP,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., June 28, 1910.

# THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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## EDITORIALS.

### ADVANCE NEW ENGLAND CHEMISTRY.

ADVANCE NEW ENGLAND is a monthly magazine, published by the Boston Chamber of Commerce, devoted to the commerce, industry and public interests of Boston and New England, whose editor is Mr. Richard J. Walsh. Some of the best known New England chemists have seized upon the August, 1910, number of this journal and with bold hands have hoisted their chemical colors and proclaimed to all their readers what chemistry may do for New England. On the outside front cover appears a cut of the plant of the Badische Anilin- und Soda-Fabrik at Ludwigshafen-on-the-Rhine and we are told editorially that in the development of this plant New England should find an inspiration. "For when the Fatherland was bare of raw materials, German genius imported them from England, manufactured them at home and sent them back to England, killing that country's own aniline industry." New England is to a large extent devoid of raw materials for the chemical industries but she is thrifty. She is already largely dependent on outside sources of raw material for her mechanical manufacturers. In applied chemistry why may she not do what Germany or any country has done?

Alan A. Claflin contributes "The Relation of Chemistry to Industry" and "Extension of Chemical Industry in New England;" F. G. Stantial, "The Chemical Resources of New England;" S. W. Wilder, "Chemical Industry in New England To-day;" Arthur D. Little, "Chemistry and Dividends" and "Chemical Fakes;" William H. Walker, "Achievements of Some New England Chemists;" Henry P. Talbot, "New England's Share in Training Chemists." In addition to this admirable array of authors and papers are several excellent editorials, all on chemical subjects. This is a chemical number indeed and a mine of information for the layman in regard to the nature of the operations of modern applied chemistry. We hope the magazine will find a wide circle of readers and that other journals will follow the same idea and issue a chemical number now and again.

### CHEMICAL ENGINEERING EDUCATION.

THE report of the Committee of the American Institute of Chemical Engineers on Chemical Engineering Education,<sup>1</sup> written by the chairman of the committee, Dr. F. W. Frerichs, of St. Louis, is of more than usual interest and offers a number of suggestions for careful consideration. The difference between American and European conditions of manufacture are ably set forth in the report and the accompanying letters; also the differences in methods and results in European and American schools and universities. Always susceptible to criticism and with abundant critics, curricula can be progressively modified only after the most careful consideration of all the facts. A committee of this sort, however, speaks with authority. It is composed of university-trained men who have had the benefit of long experience in the schools of business, manufacture, and the practising professions. Dr. Frerichs himself is a type of the scholarly chemical manufacturer. The report is worth the careful study of both educators and chemists in the industries.

## ORIGINAL PAPERS.

### ALLOYS OF NICKEL AND COBALT WITH CHROMIUM.

By ELWOOD HAYNES.

Received August 12, 1910.

The metals nickel and cobalt have always possessed a peculiar interest for the chemist. Like nearly all

<sup>1</sup> See page 430 of this issue.



of the more recently discovered metals, their compounds were known before the metals themselves were discovered. Indeed, it has been known for centuries that certain substances were capable of giving a blue color to glass, and there is but little doubt that this peculiar power was due to some crude compound of cobalt.

About two centuries ago, the ores of cobalt and nickel were encountered in the mining of copper. It was at first supposed that they were ores of the latter metal, but the miners, after vainly striving to smelt the ore, and failing to obtain any copper from it, designated it as "kupfernick," and from this expression the word "nickel" originated.

Attempts were also made to smelt the ores of cobalt, but as no useful metal resulted, they decided that the goblin, or "kobold," supposed to inhabit the mines, had placed a ban upon the ore, and thus rendered it incapable of producing valuable metal. From this designation, by the German miners, the name "cobalt" was derived.

It was not until 1751 that Cronsted published the results of an investigation which he had made upon an ore obtained from the mines of Helsingland. This ore yielded a brittle metal, and as it occurred most abundantly in "kupfernickel," he suggested for it the name of nickel.

A few years later, in 1776, it was discovered that nickel was evidently one of the constituents of a Chinese alloy, known as "packfong."

The use of nickel in German silver began about the year 1823. It was not, however, until 1857 that Messrs. Deville and Debray, the celebrated French chemists and metallurgists, prepared pure nickel by heating its oxalate in a lime crucible. From the pure metal thus obtained wires were made, which showed a tensile strength superior to that of wrought iron. The wires also showed considerable toughness, and when polished presented a bright, silvery appearance, and retained their luster for an indefinite period, under all ordinary atmospheric conditions.

A few years later the art of electroplating nickel was discovered and has since received a very wide application. Tons of the double sulphate of nickel and ammonium are used for this purpose every year.

Besides this latter important application of the metal, it is now used in large quantities for the manufacture of nickel steel, which has become a common substance in the making of naval guns, projectiles, armor plate, and high-class automobiles.

The history of cobalt is similar to that of nickel, excepting that the compounds of cobalt were used in the arts, instead of the metal itself. In fact, but little was known of the metal until 1857, when Deville produced the pure metal in practically the same manner that nickel was prepared. It was found

that cobalt was even stronger than nickel, possessing a tensile strength of about 65,000 pounds per square inch. Indeed, up to that time, it was the strongest pure metal yet discovered, and it still holds this position, with the possible exception of tantalum.

About the year 1895 I made a number of tentative experiments relating to the production of alloys of nickel with iron, chromium, and other metals. The fusions were made in small graphite crucibles, which were heated in a blast furnace of the Fletcher type, operated by natural gas. I had at that time the advantage of natural gas at a pressure of forty pounds or more per square inch. With a suitably arranged furnace of this character, temperatures ranging up to the fusing point of the most refractory Missouri fire clay were readily obtained. I succeeded in obtaining by this means alloys of nickel and chromium, which contained, however, a considerable amount of carbon and silicon. A small quantity of aluminum was sometimes added to the alloy in order to improve its quality. By this means I obtained an alloy of chromium, nickel, and aluminum, which was hard and brittle, but possessed fairly good color and luster. For this alloy a knife blade was formed, which showed fair cutting qualities and considerable resistance to atmospheric conditions. It was readily soluble in nitric acid and after long exposure to the atmosphere of a chemical laboratory it became tarnished, showing a greenish coating on its surface.

Later, I attempted to produce alloys of nickel and chromium with titanium, by means of an electric furnace, made from blocks of quicklime. This proved unsatisfactory, but I continued experimenting with the gas furnace and, finally, succeeded in producing an alloy of nickel and chromium entirely free from carbon by heating the pure mixed oxides of the two metals with powdered aluminum, in a crucible lined with pure oxide of aluminum. The reaction was so violent that most of the metal was thrown from the crucible. A few small pellets were saved, and these showed great malleability, flattening readily under the hammer, without cracking. The alloy possessed a fine color, and when polished exhibited a beautiful luster. Larger pellets were soon obtained, and it was found that when the chromium content much exceeded ten per cent. that the alloy showed remarkable resistance to chemical reagents, particularly to nitric acid.

At about the same time I reduced a mixture of the sesquioxides of cobalt and chromium with powdered aluminum and thus obtained minute pellets of an alloy of cobalt and chromium. The little particles thus produced were not much larger than pinheads. They were found to be remarkably hard and could scarcely be scratched by a file. A few of them were ground off on one side by means of carborundum and showed a brilliant luster. It occurred to me that

the metal might become serviceable for cutting instruments.

A short time after the above experiments were made I was called actively into the automobile business, and thus compelled to abandon further experiments along this line for some time.

In 1905 I repeated some of the former experiments, with a view to utilizing the alloys of cobalt and nickel with chromium for ignition points, in connection with gas engines. I was soon able to produce both the alloys of nickel and cobalt in considerable quantity. I ascertained that the nickel-chromium alloy could be worked cold, while the cobalt-chromium alloy must be worked hot in order to obtain any degree of satisfaction.

The first pellets of the cobalt-chromium alloy, weighing from fifteen to thirty grams, were obtained by heating mixtures of aluminum with the oxides of cobalt and chromium in crucibles lined with the oxide of aluminum. Some of these pellets were heated to redness and flattened out under the hammer, and while this could be done without cracking the alloy, the metal was found to be very hard even at red heat.

I soon found that it was impracticable to reduce the alloy in this manner in large quantities. I accordingly purchased a considerable amount of pure cobalt and pure chromium and had a mixture of nearly equal parts of these metals fused in an electric furnace, the metals being placed in a carbon crucible lined with pure magnesia. The alloy was cast into a small bar, about one-fourth of an inch square, and five or six inches long. This alloy exhibited most of the characteristics of that obtained by reduction with aluminum, but it could not be drawn to any extent under the hammer without cracking. Whether this was due to the high percentage of chromium, or to slight impurities in the metals employed, I am as yet unable to say.

In order to determine what the effect of alloying the cobalt with smaller percentage of chromium would be, I again had recourse to the gas furnace and succeeded in melting a mixture containing 75 per cent. cobalt and 25 per cent. chromium in a crucible made of a very refractory material, which I compounded for the purpose. Much to my satisfaction, I succeeded in melting this alloy to a perfect fluid and poured it into an ingot mold, which gave me a bar of metal about one-half an inch square and five or six inches in length. This metal proved to be very sonorous and elastic, and if some care were used it could be hammered out into a rough strip.

After a considerable amount of experimenting with various purifying agents I finally succeeded in producing a very tough and malleable alloy, which could be hammered out into the thinnest sheet at a bright red heat without showing any sign of cracking. A razor blade was made from a bar of this alloy,

and while it did not prove equal to the best steel for this purpose, it has been used hundreds of times for shaving purposes, and after a year and a half shows practically no signs of wear, though, of course, it has been necessary to strop it frequently in order to keep it in good condition. The bar was made about two years ago, and I am sure that I have since produced metal that would be much more satisfactory for the purpose.

A test of tensile strength and elastic limit of this material was made, with results as follows: Elastic limit, 79,000 lbs., tensile strength 96,000 lbs. Elongation, 3 per cent. It will be seen from the above that both the elastic limit and tensile strength of this material are superior to those of untreated steel, resembling more nearly those of good nickel steel. The elongation is quite low, but this is to be expected on account of the great hardness of the alloy, which is equal to that of mild tempered tool steel. A test was also made of the modulus of elasticity of this material, which was found to be about equal to that of steel. This is a very significant fact, since heretofore it has not been possible, so far as I am aware, to form an alloy of non-ferrous metals, which would show a modulus of elasticity comparable to that of iron and steel. And it is lack of this valuable property in various non-ferrous mixtures which renders them inferior to iron for many important purposes.

A pocket knife blade and several table knife blades were made from this material, and were found to be very satisfactory in every respect. One of these table knife blades has now been in use for more than two years in the kitchen, where it was used for all sorts of purposes, such as cutting bread, turning gridle cakes, peeling and paring vegetables, and for various other purposes such as are known only to the culinary art. After all this use and abuse, the knife shows not the slightest trace of tarnish, and has held its luster so well that when exposed to the sun it shows a reflection which dazzles the eyes.

By mixing the alloy with small quantities of other substances, its properties may be modified to a remarkable degree. By this means I have obtained alloys, or combinations, which, while very brittle, would readily scratch quartz crystal.

By reducing the quantity of chromium to some extent, and adding certain other materials, alloys which are practically proof against nitric acid can readily be obtained, which are sufficiently soft and malleable to be worked cold, having a hardness not much greater than that of mild, untempered steel.

Between these two extremes a great variety of combinations can be made which are suitable for use for various purposes. For example, I have produced an alloy of sufficient hardness that when it is formed into a small bar, say one-half an inch wide, one-fourth

an inch thick, and three inches long, and one of the ends shaped for a cold chisel, a 20-penny nail can be cut in two without marring the edge of the chisel in the slightest degree. I have formed another alloy into a small lathe tool, about one-fourth an inch square and three inches long, which showed cutting qualities comparable to high-speed tool steel. In fact, in some respects, especially under high speed and light cuts, it has stood the test for a long time, where high-speed steel failed almost instantly, on account of the intense heat generated. I wish it distinctly understood, however, that I do not recommend this material as yet for lathe tools, though it would have a high value for this purpose if it were not obliged to compete with alloy steels.

An alloy of 75 per cent. cobalt and 25 per cent. chromium, to which small quantities of other metals are added, is not only sufficiently hard for good edge tools, but is quite tough, and can be bent much beyond its elastic limit without cracking, resembling in this respect the alloy steels, but, generally speaking, it is much harder. A bar of the alloy, one-fourth inch square, can be bent at right angles without showing any signs of cracking.

*Chemical Properties.*—When the mixture of cobalt and chromium is heated to whiteness in a crucible, the cobalt first commences to fuse and immediately begins to combine with the chromium, and if the metals are mixed in the proportion of about three parts, by weight, of cobalt to one of chromium, a eutectic is formed which seems to possess a lower melting point than either cobalt or chromium.

The color of the alloy lies between that of steel and silver, and is especially pleasing in bright light. The alloy is also readily polished, but requires special treatment in order to develop its highest luster.

The most remarkable property of this combination, however, is its resistance to corrosion. It is equaled in this respect only by gold and the metal of the platinum group. It is attacked slowly by dilute hydrochloric acid and somewhat vigorously by the strong acid, especially when heated. Momentary exposure, however, to either dilute or strong hydrochloric acid has practically no effect on the metal. Both strong and dilute sulphuric acid attack it very slowly when cold, and not very rapidly even when heated. Nitric acid is totally without action upon it, and a polished piece of the alloy may be boiled in that substance for hours without affecting the luster of the metal in the slightest degree.

Solutions of the caustic alkalies are also totally without action upon it, even when boiled for hours. The alloy is likewise proof against all atmospheric influences, whether the air be moist or dry, and retains its brilliant luster for months, or even years, under severest conditions. Even sulphuretted hydro-

gen, when present in the atmosphere in large quantity, is totally without action upon it.

Its resistance to culinary operations has already been mentioned.

When the metal is heated in contact with the atmosphere it retains its color up to a temperature approaching a dull red, or about 500°, when it shows a faint straw color, which deepens as the temperature rises, passing through bronze-yellow, purple, blue, and finally terminating in blue-black.

The alloy shows no scale, even when heated to bright orange, and the film of oxides does not seem to increase in thickness after prolonged heating.

It can readily be melted in an open crucible in a gas furnace with practically no oxidation, so long as a slightly reducing flame is maintained. This is all the more remarkable on account of its high melting point, which seems to be about 1650° cc. for the 25 per cent. alloy. Indeed, the metal has been melted in this manner with a loss of less than one-half of one per cent.

*Uses.*—The uses for any substance may be limited in several particulars: first, by the limitations of its fitness; second, by the possibility of producing it in proper form; and third, by its cost. This material is particularly suitable for all kinds of small cutting instruments, since it takes an edge comparable to that of tempered steel. It is especially adaptable to the manufacture of pocket knives, on account of the beauty of its color, and the brilliancy of its luster, both of which remain permanent under all circumstances, thus giving the blades a particularly attractive appearance. Knives of this description may be used for cutting fruit without danger of marring their luster in the slightest degree.

Alloys in certain proportions will also doubtless find a wide use for surgical instruments, since they resist perfectly all sterilizing solutions.

The alloy is perhaps better adapted for table cutlery than anything that has ever yet been produced. We all know too well that a silver-plated knife, for example, is ill adapted for cutting meat, and it cannot be sharpened without destroying the plating. Steel knives, on the other hand, while they cut well, require endless labor to keep them in presentable condition, and at best, they are unsightly in appearance.

The alloy is also of considerable interest to the chemist and physicist. It is admirably adapted for the manufacture of fine weights for balances, scrapers, spatulas, and other laboratory appliances. To the physicist, it furnishes a material which is at once hard, lustrous and untarnishable, and hence well adapted for the manufacture of fine weights, measuring instruments, and various small tools.

The alloy is also particularly well adapted for the manufacture of standard weights and measures, such as the gram, kilogram, meter, etc., and it is



difficult to see in what respect it is inferior for this purpose to the expensive platinum-iridium alloy now in use.

The alloy could readily be made into laboratory vessels, cooking utensils, spoons, forks, etc., and it is limited in this respect only by its cost.

*Cost.*—Regarding the cost of production and manufacture, I am not at present prepared to make definite statements. I have succeeded, however, not only in obtaining the raw material at lower prices, but have also reduced the cost of production to a considerable degree, so that it is now possible to produce the alloys with as much despatch and precision as is possible in the production of common alloys.

KOKOMO, IND.

## THE DETERMINATION OF SUGAR LOST BY ENTRAINMENT FROM EVAPORATORS.

By R. S. NORRIS.

Received August 5, 1910.

Wherever evaporating apparatus that was constructed twenty years or more ago is in use in sugar factories, there is likely to be a continual loss, more or less, of sugar by entrainment. It was only about that time that the importance of having large vapor pipes and considerable space above the steam chest or tubes was beginning to be realized. Even recently constructed evaporators may also entrain at certain times. Some reliable method of determining how much sugar is lost in this way is therefore of importance.

In a multiple effect evaporator the entrainment is most pronounced from the last body, on account of the greater volume of the vapor and the greater viscosity of the juice. And as whatever juice is carried

out with the vapor from this effect finds its way into the condenser water, it becomes necessary to determine the sugar in a very dilute solution and to know the weight of the solution, that is, of the condenser water. Various devices have also been used for collecting a sample of the vapor, leaving the last effect representing an aliquotic portion of it, and determining the sugar in this; but these are of doubtful value.

As no detailed description of a method for determining the sugar in the condenser water is known to the writer, he has thought it advisable to publish a description of a method used by him in testing a number of evaporators.

The apparatus necessary for the determination is a stove or heater of some kind that can evaporate a considerable volume of water in a short time, a large vessel for evaporating the water in a small evaporating dish holding about two hundred cubic centimeters, a piece of sheet asbestos about eight inches (20 cm.) square, a measuring cylinder or flask holding five hundred cubic centimeters or a liter, a centigrade thermometer, and the usual sugar laboratory outfit for polarizations.

Five liters of condenser water are collected, a liter at a time, at intervals of half an hour, as it leaves the condenser and as near to it as possible, and placed in a perfectly clean vessel—preferably one that has not had anything containing sugar in it before. The evaporation had best be begun as soon as the first sample is collected, a few drops of sodium carbonate solution being first added. When the water has been evaporated down to about 150 cc. it is transferred to the small evaporating dish, the last traces being washed out of the large dish into the smaller one.

WEIGHT OF CONDENSER WATER CORRESPONDING TO A UNIT WEIGHT OF WATER EVAPORATED FROM JUICE.

Temp. of water going into con- denser in ° C.		(For Single Effects, i. e., Vacuum Pans.) Temperature of Water Coming Out of Condensers in ° C.																	
		30.	32.	34.	36.	38.	40.	42.	44.	46.	48.	50.	52.	54.	56.	58.	60.		
5	24.7	22.8	21.3	19.9	18.7	17.6	16.7	15.8	15.0	14.3	13.7	13.1	12.6	12.1	11.6	11.2			
6	25.6	23.7	22.0	20.0	19.2	18.1	17.1	16.2	15.4	14.7	14.0	13.4	12.8	12.3	11.8	11.4			
7	26.7	24.6	22.8	21.2	19.8	18.6	17.6	16.6	15.8	15.0	14.3	13.7	13.1	12.5	12.0	11.6			
8	27.9	25.6	23.6	21.9	20.4	19.2	18.0	17.0	16.1	15.3	14.6	13.9	13.3	12.8	12.3	11.8			
9	29.2	26.8	24.5	22.7	21.1	19.8	18.6	17.5	16.6	15.7	14.9	14.2	13.6	13.0	12.5	12.0			
10	30.6	27.8	25.5	23.5	21.8	20.4	19.1	18.0	17.0	16.1	15.3	14.6	13.9	13.3	12.7	12.2			
11	32.1	29.1	26.5	24.4	22.6	21.0	19.7	18.5	17.4	16.5	15.7	14.9	14.2	13.6	13.0	12.5			
12	33.9	30.5	27.7	25.4	23.4	21.8	20.3	19.0	17.9	16.9	16.0	15.2	14.5	13.9	13.3	12.7			
13	35.8	32.0	29.0	26.5	24.3	22.5	21.0	19.6	18.4	17.4	16.4	15.6	14.8	14.2	13.5	12.9			
14	38.0	33.7	30.4	27.6	25.3	23.4	21.7	20.2	19.0	17.9	16.9	16.0	15.2	14.5	13.8	13.2			
15	40.4	35.7	31.9	28.9	26.4	24.2	22.5	20.9	19.6	18.4	17.3	16.4	15.6	14.8	14.1	13.5			
16	43.2	37.8	33.6	30.3	27.5	25.2	23.3	21.6	20.2	18.9	17.8	16.8	15.9	15.1	14.4	13.8			
17	46.5	40.3	35.6	31.8	28.8	26.3	24.2	22.4	20.8	19.5	18.3	17.3	16.3	15.5	14.7	14.1			
18	50.3	43.1	37.8	33.5	30.2	27.4	25.1	23.2	21.6	20.1	18.9	17.7	16.8	15.9	15.1	14.4			
19	54.8	46.3	40.2	35.4	31.7	28.7	26.2	24.1	22.3	20.8	19.4	18.3	17.2	16.3	15.4	14.7			
20	60.1	50.1	43.0	37.6	33.4	30.1	27.3	25.1	23.1	21.5	20.0	18.8	17.7	16.7	15.8	15.0			
21	66.7	54.6	46.2	40.0	35.3	31.6	28.6	26.1	24.0	22.2	20.7	19.3	18.2	17.2	16.2	15.4			
22	74.9	59.9	49.9	42.8	37.5	33.3	30.0	27.2	25.0	23.1	21.4	20.0	18.7	17.6	16.7	15.8			
23	85.5	66.5	54.4	46.0	39.9	35.2	31.5	28.5	26.0	23.9	22.2	20.6	19.3	18.1	17.1	16.2			
24	99.6	74.7	59.7	49.8	42.7	37.3	33.2	29.9	27.2	24.9	23.0	21.3	19.9	18.7	17.6	16.6			
25	119.3	85.2	66.3	53.2	45.9	39.8	35.1	31.4	28.4	25.9	23.9	22.1	20.6	19.2	18.1	17.0			
26	148.8	98.2	74.4	59.5	49.6	42.5	37.2	33.1	29.8	27.1	24.8	22.9	21.3	19.8	18.6	17.5			
27	198.1	118.9	84.9	65.8	54.0	45.7	39.6	35.0	31.3	28.3	25.8	23.8	22.0	20.5	19.2	18.0			
28	...	148.3	98.9	74.2	59.3	49.4	42.4	37.1	33.0	29.7	27.0	24.7	22.8	21.2	19.8	18.5			
29	...	197.4	118.5	84.6	65.6	53.9	45.6	39.5	34.8	31.2	28.2	25.8	23.7	21.9	20.4	19.1			
30	...	...	147.8	98.6	73.9	59.1	49.3	42.2	37.0	32.9	29.6	26.9	24.6	22.7	21.1	19.7			

## WEIGHT OF CONDENSER WATER CORRESPONDING TO A UNIT WEIGHT OF WATER EVAPORATED FROM JUICE

(For Double Effects.)

Temp. of water going into con- denser in °C.	Temperature of water coming out of condenser in °C.															
	31.	32.	34.	36.	38.	40.	42.	44.	46.	48.	50.	52.	54.	56.	58.	60.
5	13.2	12.2	11.3	10.6	10.0	9.4	8.9	8.4	8.0	7.6	7.3	7.0	6.7	6.5	6.2	6.0
6	13.7	12.6	11.7	10.9	10.3	9.7	9.1	8.6	8.2	7.8	7.5	7.2	6.9	6.6	6.3	6.1
7	14.3	13.1	12.1	11.3	10.6	9.9	9.4	8.9	8.4	8.0	7.6	7.3	7.0	6.7	6.4	6.2
8	14.9	13.6	12.6	11.7	10.9	10.2	9.6	9.1	8.6	8.2	7.8	7.4	7.1	6.8	6.6	6.3
9	15.6	14.2	13.1	12.1	11.3	10.5	9.9	9.3	8.8	8.4	8.0	7.6	7.3	7.0	6.7	6.4
10	16.3	14.8	13.6	12.5	11.7	10.9	10.2	9.6	9.1	8.6	8.2	7.8	7.4	7.1	6.8	6.5
11	17.2	15.5	14.2	13.0	12.1	11.2	10.5	9.9	9.3	8.8	8.4	8.0	7.6	7.2	6.9	6.6
12	18.1	16.3	14.8	13.5	12.5	11.6	10.8	10.2	9.6	9.0	8.6	8.1	7.7	7.4	7.1	6.8
13	19.1	17.1	15.5	14.1	13.0	12.0	11.2	10.5	9.8	9.3	8.8	8.3	7.9	7.6	7.2	6.9
14	20.3	18.0	16.2	14.7	13.5	12.5	11.6	10.8	10.1	9.5	9.0	8.5	8.1	7.7	7.4	7.1
15	21.6	19.0	17.0	15.4	14.1	12.9	12.0	11.2	10.4	9.8	9.2	8.7	8.3	7.9	7.5	7.2
16	23.1	20.2	17.9	16.2	14.7	13.5	12.4	11.5	10.7	10.1	9.5	9.0	8.5	8.1	7.7	7.3
17	24.8	21.5	19.0	17.0	15.4	14.0	12.9	11.9	11.1	10.4	9.8	9.2	8.7	8.3	7.9	7.5
18	26.8	23.0	20.1	17.9	16.1	14.6	13.4	12.4	11.5	10.7	10.1	9.5	8.9	8.5	8.1	7.7
19	29.1	24.7	21.4	18.9	16.9	15.3	14.0	12.9	11.9	11.1	10.4	9.7	9.2	8.7	8.2	7.8
20	32.1	26.8	22.9	20.1	17.8	16.1	14.6	13.4	12.3	11.5	10.7	10.0	9.4	8.9	8.4	8.0
21	35.6	29.1	24.7	21.4	18.8	16.9	15.3	13.9	12.8	11.9	11.1	10.3	9.7	9.2	8.7	8.2
22	40.0	32.0	26.7	22.9	20.0	17.8	16.0	14.5	13.3	12.3	11.4	10.7	10.0	9.4	8.9	8.4
23	45.6	35.5	29.0	24.6	21.3	18.8	16.8	15.2	13.9	12.8	11.8	11.0	10.3	9.7	9.1	8.6
24	53.2	39.9	31.9	26.6	22.8	19.9	17.7	15.9	14.5	13.3	12.2	11.4	10.6	10.0	9.4	8.9
25	63.7	45.5	35.4	28.9	24.5	21.2	18.7	16.8	15.2	13.8	12.7	11.8	11.0	10.3	9.6	9.1
26	79.5	53.0	39.7	31.8	26.5	22.7	19.9	17.7	15.9	14.4	13.2	12.2	11.4	10.6	9.9	9.3
27	.....	63.5	45.3	35.1	28.8	24.4	21.2	18.7	16.7	15.1	13.8	12.7	11.8	10.9	10.2	9.6
28	.....	79.2	52.8	38.9	31.7	26.4	22.6	19.8	17.6	15.8	14.4	13.2	12.2	11.3	10.6	9.9
29	.....	.....	63.3	44.7	35.0	28.7	24.3	21.1	18.6	16.6	15.1	13.7	12.6	11.7	10.9	10.2
30	.....	.....	78.9	52.6	39.5	31.6	26.3	22.6	19.7	17.5	15.8	14.3	13.1	12.1	11.3	10.5

## WEIGHT OF CONDENSER WATER CORRESPONDING TO A UNIT WEIGHT OF WATER EVAPORATED FROM JUICE.

(For Triple Effect.)

Temp. of water going into con- denser in °C.	Temperature of water coming out of condenser in °C.															
	31.	32.	34.	36.	38.	40.	42.	44.	46.	48.	50.	52.	54.	56.	58.	60.
5	9.1	8.4	7.9	7.4	6.5	6.5	6.2	5.8	5.6	5.3	4.9	4.9	4.7	4.5	4.3	4.2
6	9.5	8.7	8.1	7.6	7.1	6.7	6.3	6.0	5.7	5.4	5.2	5.0	4.7	4.6	4.4	4.2
7	9.9	9.1	8.4	7.8	7.3	6.9	6.5	6.1	5.8	5.5	5.3	5.1	4.8	4.6	4.3	4.3
8	10.3	9.5	8.7	8.1	7.6	7.1	6.7	6.3	6.0	5.7	5.4	5.2	4.9	4.7	4.5	4.4
9	10.8	9.9	9.1	8.4	7.8	7.3	6.9	6.5	6.1	5.8	5.5	5.3	5.0	4.8	4.6	4.4
10	11.3	10.3	9.4	8.7	8.1	7.5	7.1	6.7	6.3	6.0	5.7	5.4	5.1	4.9	4.7	4.5
11	11.9	10.8	9.8	9.0	8.4	7.8	7.3	6.8	6.5	6.1	5.8	5.5	5.3	5.0	4.8	4.6
12	12.5	11.3	10.2	9.4	8.7	8.1	7.5	7.0	6.6	6.3	5.9	5.6	5.4	5.1	4.9	4.7
13	13.2	11.8	10.7	9.8	9.0	8.3	7.8	7.3	6.8	6.4	6.1	5.8	5.5	5.2	5.0	4.8
14	14.0	12.5	11.2	10.2	9.4	8.6	8.0	7.5	7.0	6.6	6.2	5.9	5.6	5.4	5.1	4.9
15	15.0	13.2	11.8	10.7	9.8	9.0	8.3	7.7	7.2	6.8	6.4	6.1	5.8	5.5	5.2	5.0
16	16.0	14.0	12.4	11.2	10.2	9.3	8.6	8.0	7.5	7.0	6.6	6.2	5.9	5.6	5.3	5.1
17	17.2	14.9	13.2	11.8	10.6	9.7	8.9	8.3	7.7	7.2	6.8	6.4	6.0	5.7	5.5	5.2
18	18.6	15.9	14.0	12.4	11.2	10.1	9.3	8.6	8.0	7.4	7.0	6.6	6.2	5.9	5.6	5.3
19	20.3	17.1	14.9	13.1	11.7	10.6	9.7	8.9	8.3	7.7	7.2	6.8	6.4	6.0	5.7	5.4
20	22.2	18.5	15.9	13.9	12.4	11.1	10.1	9.3	8.6	8.0	7.4	7.0	6.5	6.2	5.9	5.6
21	24.7	20.2	17.1	14.8	13.1	11.7	10.6	9.7	8.9	8.2	7.7	7.2	6.7	6.4	6.0	5.7
22	27.7	22.2	18.5	15.8	13.9	12.3	11.1	10.1	9.2	8.5	7.9	7.4	6.9	6.5	6.2	5.8
23	31.6	24.6	20.1	17.0	14.8	13.0	11.7	10.5	9.6	8.9	8.2	7.6	7.2	6.7	6.3	6.0
24	36.8	27.6	22.1	18.4	15.8	13.8	12.3	11.1	10.1	9.2	8.5	7.9	7.4	6.9	6.5	6.1
25	44.1	31.5	24.5	20.1	17.0	14.7	13.0	11.6	10.5	9.6	8.8	8.2	7.6	7.1	6.7	6.3
26	55.1	36.7	27.5	22.0	18.4	15.7	13.8	12.2	11.0	10.0	9.2	8.5	7.9	7.4	6.9	6.5
27	73.3	46.0	31.4	24.4	20.0	16.9	14.7	12.9	11.6	10.5	9.6	8.8	8.2	7.6	7.1	6.6
28	.....	54.9	36.6	27.4	22.0	18.3	15.7	13.7	12.2	11.0	10.0	9.2	8.6	7.9	7.3	6.9
29	.....	.....	43.8	31.3	24.3	19.9	16.9	14.6	12.9	11.5	10.4	9.5	8.8	8.1	7.6	7.1
30	.....	.....	54.7	36.5	27.4	21.9	18.2	15.6	13.7	12.2	11.0	10.0	9.1	8.4	7.8	7.3

The small dish is placed on the stove over the sheet of asbestos with a two and a half-inch (6 cm.) hole in it. The evaporation is continued until only about 75 cc. remain—it is not safe to go beyond this on account of the risk of decomposing some of the sugar. The solution is then transferred to a 100 cc. sugar flask, about 1 cc. of lead subacetate solution and a little aluminum cream added, made up to 110 cc., filtered and polarized. The polarization of the solution can be found from Schmitz's table, taking the first reading on the left in the table. To find the polarization of the condenser water from this, divide

by fifty, since the water was evaporated to one-fiftieth of its original volume.

For instance, suppose the polariscope reading were 3.0, the 100 cc. of evaporated solution would then have a polarization of 0.85 and the original condenser water a polarization of 0.017.

In order to interpret this in pounds of sugar lost in condenser water per day, it is only necessary to know the weight of condenser water. This can be calculated from the volume measured with a weir, or it can be found in terms of the weight of juice by taking the temperature of the water going in and

## WEIGHT OF CONDENSER WATER CORRESPONDING TO A UNIT WEIGHT OF WATER EVAPORATED FROM JUICE.

(For Quadruple Effects.)

Temp. of water going into con- denser in ° C.	Temperature of water coming out of condenser in ° C.															
	30.	32.	34.	36.	38.	40.	42.	44.	46.	48.	50.	52.	54.	56.	58.	60.
5	7.0	6.5	6.0	5.6	5.3	5.0	4.7	4.5	4.3	4.1	3.9	3.7	3.6	3.4	3.3	3.2
6	7.3	6.7	6.2	5.8	5.5	5.1	4.9	4.6	4.4	4.2	4.0	3.8	3.6	3.5	3.4	3.2
7	7.6	7.0	6.5	6.0	5.6	5.3	5.0	4.7	4.5	4.3	4.1	3.9	3.7	3.6	3.4	3.3
8	7.9	7.3	6.7	6.2	5.8	5.4	5.1	4.8	4.6	4.4	4.1	4.0	3.8	3.6	3.5	3.3
9	8.3	7.6	7.0	6.4	6.0	5.6	5.3	5.0	4.7	4.5	4.2	4.0	3.9	3.7	3.6	3.4
10	8.7	7.9	7.2	6.7	6.2	5.8	5.4	5.1	4.8	4.6	4.3	4.1	3.9	3.8	3.6	3.5
11	9.1	8.3	7.5	6.9	6.4	6.0	5.6	5.3	5.0	4.7	4.4	4.2	4.0	3.9	3.7	3.5
12	9.3	8.7	7.9	7.2	6.7	6.2	5.8	5.4	5.1	4.8	4.6	4.3	4.1	3.9	3.8	3.6
13	10.2	9.1	8.2	7.5	6.9	6.4	6.0	5.6	5.2	4.9	4.7	4.4	4.2	4.0	3.9	3.7
14	10.8	9.6	8.6	7.8	7.2	6.6	6.2	5.7	5.4	5.1	4.8	4.5	4.3	4.1	4.0	3.8
15	11.5	10.1	9.1	8.2	7.5	6.9	6.4	5.9	5.6	5.2	4.9	4.7	4.4	4.2	4.1	3.9
16	12.3	10.7	9.6	8.6	7.8	7.2	6.6	6.1	5.7	5.4	5.1	4.8	4.5	4.4	4.2	4.0
17	13.2	11.4	10.1	9.0	8.2	7.5	6.9	6.4	5.9	5.5	5.2	4.9	4.6	4.4	4.2	4.0
18	14.3	12.2	10.7	9.5	8.6	7.8	7.1	6.6	6.1	5.7	5.4	5.0	4.8	4.5	4.3	4.1
19	15.6	13.2	11.4	10.1	9.0	8.1	7.4	6.8	6.3	5.9	5.5	5.2	4.9	4.6	4.4	4.2
20	17.1	14.2	12.2	10.7	9.5	8.5	7.8	7.1	6.6	6.1	5.7	5.3	5.0	4.7	4.5	4.3
21	18.9	15.5	13.1	11.4	10.0	9.0	8.1	7.4	6.8	6.3	5.9	5.5	5.2	4.9	4.6	4.4
22	21.3	17.0	14.2	12.2	10.6	9.5	8.5	7.7	7.1	6.5	6.1	5.7	5.3	5.0	4.7	4.5
23	24.3	18.0	15.4	13.1	11.1	10.0	8.9	8.1	7.4	6.8	6.3	5.9	5.5	5.1	4.9	4.6
24	28.3	21.2	17.0	14.1	12.1	10.6	9.4	8.5	7.7	7.1	6.5	6.1	5.7	5.3	5.0	4.7
25	33.9	24.2	18.8	15.4	13.0	11.3	10.0	8.9	8.1	7.4	6.8	6.3	5.8	5.5	5.1	4.8
26	42.3	28.2	21.1	16.9	14.1	12.1	10.6	9.4	8.5	7.7	7.0	6.5	6.0	5.6	5.3	5.0
27	56.3	33.8	24.1	18.7	15.3	13.0	11.3	9.9	8.9	8.0	7.3	6.8	6.3	5.8	5.4	5.1
28	.....	42.2	28.1	21.1	16.9	14.0	12.0	10.5	9.4	8.4	7.7	7.0	6.5	6.0	5.6	5.3
29	.....	.....	33.6	24.0	18.6	15.3	12.9	11.2	9.9	8.9	8.0	7.3	6.7	6.2	5.8	5.4
30	.....	.....	42.0	28.0	21.0	16.8	14.0	12.0	10.5	9.3	8.4	7.6	7.0	6.5	6.0	5.6

## WEIGHT OF CONDENSER WATER CORRESPONDING TO A UNIT WEIGHT OF WATER EVAPORATED FROM JUICE.

(For Quintuple Effects.)

Temp. of water going into con- denser in ° C.	Temperature of water coming out of condenser in ° C.															
	30.	32.	34.	36.	38.	40.	42.	44.	46.	48.	50.	52.	54.	56.	58.	60.
5	5.8	5.4	5.0	4.7	4.4	4.1	3.9	3.7	3.5	3.4	3.2	3.1	3.0	2.8	2.7	2.6
6	6.0	5.6	5.2	4.8	4.5	4.3	4.0	3.8	3.6	3.4	3.3	3.1	3.0	2.9	2.8	2.7
7	6.3	5.8	5.3	5.0	4.7	4.4	4.1	3.9	3.7	3.5	3.4	3.2	3.1	3.0	2.8	2.7
8	6.6	6.0	5.5	5.1	4.8	4.5	4.2	4.0	3.8	3.6	3.4	3.3	3.1	3.0	2.9	2.8
9	6.9	6.3	5.8	5.3	5.0	4.6	4.4	4.1	3.9	3.7	3.5	3.3	3.2	3.1	2.9	2.8
10	7.2	6.5	6.0	5.5	5.1	4.8	4.5	4.2	4.0	3.8	3.6	3.4	3.3	3.1	3.0	2.9
11	7.5	6.8	6.2	5.7	5.3	4.9	4.6	4.3	4.1	3.9	3.7	3.5	3.3	3.2	3.1	2.9
12	8.0	7.2	6.5	6.0	5.5	5.1	4.8	4.5	4.2	4.0	3.8	3.6	3.4	3.3	3.1	3.0
13	8.4	7.5	6.8	6.2	5.7	5.3	4.9	4.6	4.3	4.1	3.9	3.7	3.5	3.3	3.2	3.0
14	8.9	7.9	7.1	6.5	5.9	5.5	5.1	4.8	4.5	4.2	4.0	3.8	3.6	3.4	3.2	3.1
15	9.5	8.4	7.5	6.8	6.2	5.7	5.3	4.9	4.6	4.3	4.1	3.9	3.7	3.5	3.3	3.2
16	10.2	8.9	7.9	7.1	6.5	5.9	5.5	5.1	4.7	4.4	4.2	4.0	3.7	3.6	3.4	3.2
17	10.9	9.5	8.4	7.5	6.8	6.2	5.7	5.3	4.9	4.6	4.3	4.1	3.8	3.6	3.5	3.3
18	11.8	10.1	8.9	7.9	7.1	6.4	5.9	5.5	5.1	4.7	4.4	4.2	3.9	3.7	3.5	3.4
19	12.9	10.9	9.4	8.3	7.5	6.7	6.2	5.7	5.2	4.9	4.6	4.3	4.0	3.8	3.6	3.5
20	14.1	11.8	10.1	8.8	7.9	7.1	6.4	5.9	5.4	5.0	4.7	4.4	4.2	3.9	3.7	3.5
21	15.7	12.8	10.9	9.4	8.3	7.4	6.7	6.1	5.6	5.2	4.9	4.6	4.3	4.0	3.8	3.6
22	17.6	14.1	11.7	10.1	8.8	7.8	7.0	6.4	5.9	5.4	5.0	4.7	4.4	4.1	3.9	3.7
23	20.1	15.6	12.8	10.8	9.4	8.3	7.4	6.7	6.1	5.6	5.2	4.8	4.5	4.3	4.0	3.8
24	23.4	17.5	14.0	11.7	10.0	8.8	7.8	7.0	6.4	5.8	5.4	5.0	4.7	4.4	4.1	3.9
25	28.0	20.0	15.6	12.7	10.8	9.3	8.2	7.4	6.7	6.1	5.6	5.2	4.8	4.5	4.2	4.0
26	35.0	23.3	17.5	14.0	11.7	10.0	8.7	7.8	7.0	6.4	5.8	5.4	5.0	4.7	4.4	4.1
27	46.6	27.9	20.0	15.5	12.7	10.7	9.3	8.2	7.4	6.7	6.1	5.6	5.2	4.8	4.5	4.2
28	.....	34.9	23.2	17.4	13.9	11.6	10.0	8.7	7.7	7.0	6.3	5.8	5.4	5.0	4.6	4.4
29	.....	.....	27.8	19.9	15.4	12.7	10.7	9.3	8.2	7.3	6.6	6.1	5.6	5.2	4.8	4.5
30	.....	.....	34.7	23.2	17.4	13.9	11.6	9.9	8.7	7.7	6.9	6.3	5.8	5.3	5.0	4.6

coming out of the condenser with a centigrade thermometer, and referring to the accompanying tables, which give the weight of condenser water corresponding to unit weight of water evaporated from the juice. And this number multiplied by the percentage evaporation, calculated from the formula

Per cent. evaporation (by weight) =

$$\frac{\text{Brix of Evaporated Juice} - \text{Brix of Thin Juice,}}{\text{Brix of Evaporated Juice}}$$

gives the weight of condenser water corresponding to unit weight of juice entering evaporator.<sup>1</sup> This

<sup>1</sup> For convenience this may be taken to be equal to the weight of diffusion juice or mixed juice, which is usually known.

result, multiplied by the weight of mixed juice or diffusion juice for twenty-four hours, gives the weight of condenser water per day, from which the weight of sugar in the condenser water for one day can be calculated directly, by multiplying by its polarization as found above. For example, with a triple effect, suppose we have:

Temperature of water going into condenser.....	20° C.
Temperature of water coming out of condenser....	42° C.
Brix of clarified or thin juice.....	14.7
Brix of syrup or thick juice.....	62.0
Weight of mixed juice or diffusion juice in one day.	500 tons

Using these figures, we find from the table that there are 10.1 pounds of condenser water for each



pound of water evaporated from the juice. The evaporation calculated from the formula is  $76.3$  per cent. We therefore have  $10.1 \times 0.763 = 7.7$  pounds of condenser for each pound of juice. And since the diffusion, or mixed juice weighs 1,000,000 pounds, the condenser water will weigh  $1,000,000 \times 7.7 = 7,700,000$  pounds and contain  $7,700,000 \times 0.00017 = 1309$  pounds of sugar per day.

The tables were calculated from the formulas<sup>1</sup>

$$(I) W_a = \frac{w(c - t_b)}{t_b - t_a}, \quad (II) W_b = (W_a + I)E,$$

in which

$W_a$  = weight of injection water going into condenser;

$W_b$  = weight of water coming out of condenser;

$w$  = weight of vapor from last body;

$c$  = total heat of unit weight of vapor from last body, in calories;

$t_a$  = temperature in °C. of injection water going into condenser;

$t_b$  = temperature in °C. of water coming out of condenser;

$E$  = average per cent. evaporation in last body.

In calculating the tables the factor  $c$  is taken equal to 621.3, which is the total heat of unit weight of steam under a vacuum of 25 inches. The corresponding factors at other pressures are:

Inches.	Calories.
22	625.9
23	624.4
24	623.1
26	619.5
27	616.8
28	613.4

For the factor  $E$  the following numbers were used in the calculations:

Single effect.....	1.000
Double effect.....	0.534
Triple effect.....	0.370
Quadruple effect.....	0.284
Quintuple effect.....	0.235

EXPERIMENT STATION

HAWAIIAN SUGAR PLANTERS' ASSOCIATION,  
HONOLULU, T. H.

## AN ACCURATE METHOD FOR CALORIMETRIC DETERMINATIONS ON ANTHRACITE COAL.

By OSCAR W. PALMBERG

Received July 9, 1910.

As I have been called upon during the past year to make a considerable number of calorimetric determinations on anthracite coals and using an Atwater-Mahler calorimeter in all my work, it was necessary to find some convenient, reliable and accurate method to burn these coals, as it is a well-known fact that anthracite coals do not burn readily in the oxygen bomb calorimeter. No matter how finely the coal is pulverized, it is very seldom that a complete combustion can be obtained, and although I have been able to make duplicate tests which agreed very

well, in many cases, the calorimetric determinations were low and it would be necessary to filter the bomb washings and burn the residue in a Gooch crucible and from this loss in weight correct for the unburned coal. Such a method is not alone inaccurate, but requires too much time where many tests a day are to be run. The combustion in the bomb became less complete the greater the ash content. It occurred to me that the coal would have to be mixed with some material that would assist combustion and burn up this small amount of coal which was invariably left in the bomb washings. I first tried to make a pellet by mixing pulverized cane sugar with the coal and succeeded in getting rather concordant results this way from a mixture of 1 gram of sugar and 0.5 gram coal, but this method had its fault and was not very satisfactory.

Next I tried to enclose the coal (about 0.5 gram) in a gelatine capsule, but never succeeded in obtaining complete combustion; at least not with very high ash coals; and besides, gelatine being so hygroscopic, errors would occur in the weighings.

The only satisfactory and simple method I have found which gives absolutely complete combustion is to weigh out 0.2 gram of semi-bituminous coal of about 14300 to 14500 B. t. u. in a shallow nickel capsule (1 in.  $\times$  3/8 in.) which fits in the supports in the bomb conveniently, and after spreading this soft coal evenly over the bottom of the capsule, weigh on top of this 0.8 gram of the anthracite coal, pulverized to pass a 100 mesh. A little more or less in weight of either coal does not affect the result, so long as the quantity taken has been accurately weighed. This weighing can be done in a very short time and there is nothing more to do but to have the wire touch the coal, whereupon the combustion will be complete and tests can be made as accurately as on any soft coal.

It is only necessary to know the calorific content and the amount of sulphur in the kindler (soft coal) burned, whereupon the correction for these is applied very conveniently. I keep a four-ounce bottle of stock coal which has been passed through a 60-mesh sieve and thoroughly mixed and from this draw a small specimen tube full, which tube full will last for about 50 determinations.

My stock bottle of coal was put up June 4, 1909, and calorimetric tests were made from time to time to make sure of the corrections and the following results were obtained:

Test on coal as burned.	Dry basis.	Date of test.
7942 Calories	14338 B. t. u.	June 4, 1909
7952 Calories	14349 B. t. u.	June 18, 1909
7954 Calories	14359 B. t. u.	Aug. 3, 1909
7936 Calories	14332 B. t. u.	Feb. 5, 1910
7920 Calories	14300 B. t. u.	Feb. 16, 1910
7899 Calories	14260 B. t. u.	Mar. 26, 1910
7915 Calories	14283 B. t. u.	Apr. 20, 1910
7927 Calories (used 1/2 gram coal)	14297 B. t. u.	Apr. 26, 1910
7923 Calories (used 1 gram coal)	14298 B. t. u.	Apr. 26, 1910

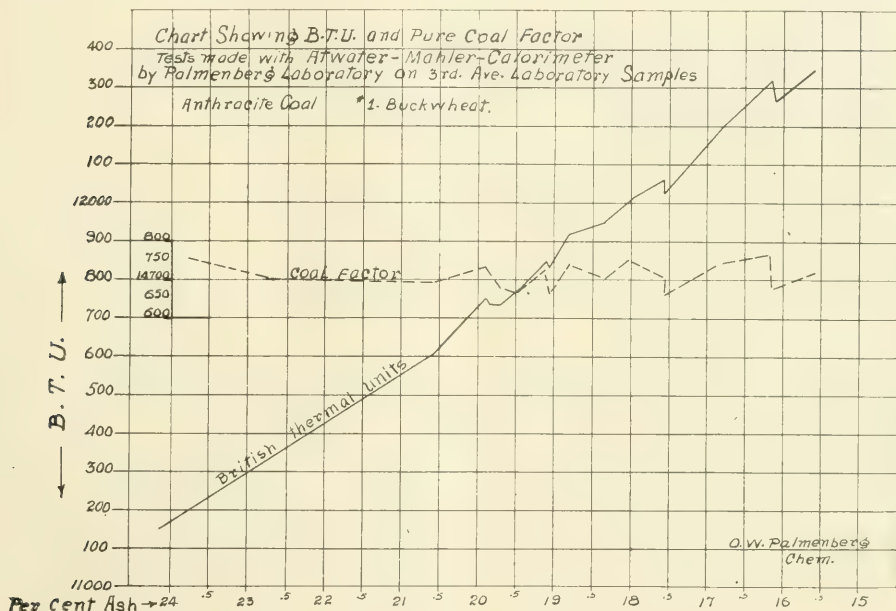
<sup>1</sup> For a discussion of formula I see E. Hausbrand, "Evaporating, Condensing and Cooling Apparatus," p. 212.

There seems to be a gradual decrease in the thermal content of the coal, due probably to oxidation, but on the whole very little change has taken place and not enough to make any appreciable error in the determination when running the anthracite. The variations in the above results are probably due, in part, to the fact that the moisture determination was not made with each new calorific determination. Thus the first four B. t. u. figures were calculated from the calorific test, using the moisture content of the first test and as the coal lost in moisture the calculation would be too high. This accounts for the apparent increase in the thermal value. On the other five tests the moisture was determined in every case.

$$H = \frac{\text{B. t. u. — Sulphur} \times 4050}{1. - (\text{Ash} + \text{S})}$$

for dry coal, and gives a very good line on the accuracy of the work where many tests are run on a coal coming from the same region. The factor in this case averages 14690, and from this it is plainly seen that the results are consistent. These two charts are practically identical, and one line would cover the other if placed over one another.

There are a few irregularities, but nothing out of the ordinary general run of work. In this case all the results were taken as obtained, not being picked with the intention of giving a symmetrical chart, and in this way the consistency of the work and



When using the coal for combustion with the anthracite, the calorific content of the coal as drawn from the tube only need be known. To show how reliable calorific tests run by this method are, when burning an anthracite in a calorimeter of the Berthelot-Mahler type, I arranged all my results on two sets of tests made on the same coal delivered to different places of consumption, in consecutive order from the lowest to the highest ash content and placed these B. t. u. figures corresponding to the ash in each sample on cross-section paper. The accompanying charts bring out this fact very plainly. The lower line represents the calorimetric test and the upper line the "Pure Coal" factor. This pure coal factor is obtained by Lord and Haas' formula,

method can be proven. The results were all taken from the general run of tests, and time did not permit to run tests over unless there was some striking error. The coal on which all these determinations were made was No. 1 buckwheat size and came from the Lehigh locality; it was shipped in 800-ton lighters to the consumer and the samples were taken automatically from the weighing hopper.

After titrating the bomb washings and acidifying, boiling and filtering, the residual ash from the solution was dried on the paper, brushed on to a watch glass and examined under the microscope, and in very few cases was there any unburned coal to be found, and if present the amount was too small to have any appreciable effect upon the test.





brought to my attention during several months of work as assayer at the Tintic Smelter.

During that time we had considerable trouble in checking with the mine assayer in our assays for silver.

The ores on which varying results were obtained were oxidized lead ores, containing from forty to sixty per cent. of silica, about five per cent. of iron and two per cent. of lime, from fifteen to forty per cent. of lead, from twenty to eighty ounces of silver, never more than two per cent. of zinc, about one per cent. of sulphur, and only a trace of copper.

The regular (stock) flux used on these ores was made up as follows:

	Lbs.
Litharge.....	12.0
Borax glass.....	2.0
Flour.....	1.1
Sodium bicarbonate.....	12.0
Potassium carbonate.....	12.0

About eighty grams of the above flux were charged with a half-assay ton of ore. The assay was made by fusion in a twenty-gram crucible, using a cover of powdered borax glass. A lead button weighing from twenty-one to twenty-four grams was thus obtained.

To minimize volatilization losses these buttons were cupelled, as far as possible, separately from buttons obtained from fusions of ores containing copper and zinc, on account of the fact that the former required a lower temperature of cupellation, particularly at the blinking point.

Three, and sometimes four, rows of cupels were charged at one time, an extra row of empty cupels being placed in front to prevent rapid temperature changes. Empty crucibles were used in the back of the muffle to regulate the heat.

The silver values which we obtained were almost invariably higher than those obtained by the mine assayer and, in case of dispute, very commonly higher than those of the umpire. This variation sometimes amounted to as much as an ounce, the splitting limit for settlement being five-tenths of an ounce.

The lower results obtained by the second and third parties I attribute to two causes:

- (1) Higher temperature of cupellation.
- (2) Excessive amounts of litharge in the fluxes.

With regard to temperature of cupellation, I understand that it is rather common practice in some assay offices, in running control and umpire work, to cupel in single rows. In so doing the cupels often show much heavier "feathers" on one side than on the other—evidence that the temperature was higher than necessary.

Moreover, if buttons of the character described be cupelled with buttons containing copper, the latter will require a higher cupelling temperature, involving a correspondingly greater volatilization loss in the former.

With regard to excessive use of litharge, I made up two other fluxes, similar to our own stock flux, but containing, in the first case (A) about fifty grams of litharge, and in the second case (B) seventy-five grams of litharge per half-assay ton charge.

Three ores were assayed using these different fluxes, care being taken to cupel buttons from different fluxes in the same muffle, so that the temperature of cupellation should be as nearly as possible the same in each case.

The average of results obtained were as follows:

	Regular flux.	Flux A.	Flux B.
Ore No. 1.....	51.05	50.86	50.62
Ore No. 2.....	42.36	42.20	42.02
Ore No. 3.....	27.82	27.70	27.55

The figures given are ounces of silver per ton of ore.

The use of litharge in excess of the amount necessary to bring down a lead button of proper size on such ores as the above is, of course, unnecessary, but such practice I find is not uncommon, especially where a regular stock flux is used, containing an excess of litharge, the function of which is, as a "cleanser," to throw any copper or other impurities into the slag.

UNIVERSITY OF UTAH.

## RAPID ESTIMATION OF AVAILABLE CALCIUM OXIDE IN LIME USED IN CYANIDE WORK.

By L. W. BAHNEY

Received August 2, 1910.

Lime is the alkali that is almost universally added to the solutions in the cyanide process of gold and silver extraction for maintaining the so-called protective alkalinity.

The value of lime for this purpose depends upon the percentage of calcium oxid which it contains, and three factors determine this.

First, purity of the limestone.

Second, degree of burning temperature and time.

Third, length of time it may have been stored and whether it has been damp or dry during this period of storage.

These three factors combine to make the quality of lime which is bought in the open market rather uncertain.

While lime bought in the United States from a reliable firm, which thoroughly burns a pure limestone and delivers at once to the consumer from the kilns, may be of a fairly high and uniform composition, yet in Mexico and Central America, where it is purchased from many small producers who often have a poor grade of limestone to start with, and whose kilns are small and crude and who use as little fuel as possible, the quality of the lime is quite variable.

The determination of calcium by the gravimetric method, with the necessity of also determining the proportion of carbon dioxide, silica and iron, requires

too much time, and is usually out of the question for the isolated plant without the necessary apparatus and the services of a skilled chemist.

The calculating of all the calcium found to calcium oxid, although sometimes done, is manifestly very inaccurate.

Several methods<sup>1</sup> of titrating by means of a standard acid have been described and no doubt give good results, which are sufficiently accurate for a technical method, and the objections to these are that they involve the preparation of a standard solution of some acid, usually *N*/10 HCl, which cannot be weighed out but must be standardized with some other standard solution. The idea suggested itself of using the solution which is employed in determining the alkalinity of the cyanide solutions.

Solutions of the following acids have been used by different operators for this purpose: sulphuric, nitric, hydrochloric and oxalic. Oxalic acid is perhaps the best for this purpose because a standard solution can be prepared by weighing the solid acid and dissolving it in water.

While this method of standardization is open to the objection that the hydration of the acid may vary somewhat, yet it yields a solution sufficiently accurate for technical work, and so far as I am aware, the use of oxalic acid for this purpose has not been suggested.

Pure calcium oxid was prepared by selecting pure white crystals of calcite, grinding fine in an agate mortar and igniting in a platinum crucible over a strong blast until constant weight resulted.

This oxid was cooled in a desiccator, then ground in an agate mortar to pass 200 mesh, and the calcium oxid determined gravimetrically; the result was 99.98 per cent. against a theoretical 100 per cent.

This calcium oxid was then used as a standard throughout the succeeding tests.

Similar weighed portions were titrated with decinormal HCl and oxalic acid, using phenolphthalein as indicator, and where 44.2 cc. of HCl were required, 44.6 cc. oxalic acid completed the reaction. The solution of the oxalic acid used in the subsequent experiments was made by dissolving 14.6068 grams in enough distilled water to make a liter. The first experiments were made upon small amounts of 140 mg., to which was added 100 cc. of water before titration, the idea being to have just enough lime present to be theoretically soluble in that amount of water.

As this is a rather small amount to handle and the method given in Treadwell and Hall,<sup>2</sup> of weighing out 14.000 grams, making 1000 cc. of emulsion, removing 100 cc., again diluting to 1000 cc., and removing 100 cc. for titration, did not give results which

checked upon low-grade limes and is open to the objection of extra manipulation, larger amounts were tried and were introduced directly into the flask in which the determination was to be carried out.

The weight of lime to be taken was calculated so that each cubic centimeter of oxalic acid solution should represent 1 per cent. of calcium oxid:

Lime	:	Lime	:	Oxalic	:	Oxalic
56.09	:		:	126.048	:	1.46068
	:	x	:		:	
	:	x equals 650	:		:	

This weight in milligrams (650) was then used in all the tests, and the following table will show results which are satisfactory for a technical method.

The titrations were made in the cold by introducing 650 mg. of the sample into a 300 cc. Erlenmeyer flask containing 50 cc. of distilled water, using phenolphthalein as indicator.

Calcium carbonate Per cent. present.	Calcium oxide.	Calcium oxide. Per cent. found
95	5	5.2
90	10	10.3
85	15	15.3
80	20	20.5
75	25	25.0
70	30	30.2
65	35	35.0
60	40	40.0
55	45	45.0
50	50	49.8
45	55	54.5
40	60	59.9
35	65	64.8
30	70	69.6
25	75	74.5
20	80	79.2
15	85	84.8
10	90	90.0
5	95	94.7
0	100	100.0

This series indicates that calcium oxid, in the presence of calcium carbonate, can be determined by this method within a fair degree of accuracy.

Silica, which is present in most limes, does not interfere.

Magnesia, which is also present in most limes, in greater or lesser amount, is very slightly soluble in water and shows a faint reaction with the indicator, but it is of no value as an alkali in cyanide work and should not be shown in a determination of the available alkali in lime to be used for this purpose.

Fortunately the point where the alkalinity due to CaO stops is readily recognized after a little practice, for the color is a vivid pink while that of MgO is faint, and the color in the titration of MgO disappears with the addition of only one- or two-tenths of a cubic centimeter of the oxalic acid solution, and the color returns very slowly and feebly while that of lime is rapid and sharp.

This is illustrated by the fact that a titration of pure CaO required only 5 minutes while the same amount of MgO required three and one-half hours.

In order to test the method in the presence of magnesia, two samples of limestone containing magnesia were ground to 200 mesh and titrated (after ignition

<sup>1</sup> Sutton's "Volumetric Analysis." "Quantitative Analysis," Vol. II. Treadwell and Hall. *Trans. Met. Soc. S. Africa.*

<sup>2</sup> Vol. II, p. 453.

in platinum crucibles to constant weight). The CaO was determined by the gravimetric method in each sample, there was no silica present and no more than a trace of iron, with these results:

	CaO present by gravimetric method.	Calcium oxid found by the oxalic acid method.
	Per cent.	Per cent.
Sample No. 1.....	57.6	57.6
Sample No. 2.....	50.4	51.0

This indicates that the magnesia does not interfere. Its presence and approximate amount can be judged by the behavior of the titration and quite accurately by continuing the titration if one can spare the time needed.

Iron oxid is sometimes present in impure limes in considerable amount and it obscures or masks the color of the indicator, but if the precipitate be allowed to subside the titration may be carried out to within 1 per cent. of the correct result.

If it is desirable to determine the amount of carbonate present in an imperfectly burned lime it may be carried on as follows:

After grinding the sample to pass 200 mesh weigh out 650 mg. and make the titration in the usual manner; call this result 1-available calcium oxid.

Now ignite some of the finely ground sample in a muffle or over a blast and make another determination, using 650 mg., calling this result No. 2.

Subtract 1 from 2 and divide by 1.78.

*Method of Procedure.*—The sample must be ground to pass through a 200-mesh screen. Into a 300 cc. Erlenmeyer flask place 50 cc. of distilled water, then add the 650 mg. of the finely ground sample, stopper the flask and shake vigorously for 10 seconds, add two drops of solution of phenolphthalein and then run in the standard solution of oxalic acid until the pink color is discharged, then place in the stopper and shake again.

When the color returns, if it is lime, it will be a bright vivid pink, and the addition of perhaps one-half cc. will be necessary to discharge this color, but if the flask is again shaken and the color returns slowly and is a faint, weak pink this is the end point for the lime.

At all time during the running in of the oxalic acid solution the flask should be shaken as violently as possible, care being taken not to allow it to splash out, so that calcium oxid will pass into solution. In nearly every instance of titrating a high-grade lime the pink color remained vivid nearly to the finish, which shows that the CaO is rapidly soluble. If a completed titration is allowed to stand for from 15 minutes to half an hour the pink color will return and show as brightly as in the beginning.

The reading of the burette is in per cent. of calcium oxid. The solutions necessary are:

Oxalic acid, 14.6068 grams of pure crystals dissolved in enough water to make a liter.

Phenolphthalein 0.5 gram dissolved in a mixture of 50 cc. alcohol and 50 cc. water.

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[CONTRIBUTION NO. 10 FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## DIFFERENTIAL CONDENSATION IN DISTILLATION AND RECTIFICATION OF BINARY LIQUID MIXTURES.

By ALCAN HIRSCH

The object of this paper is to show the important part which condensation plays in distillation and rectification of binary liquid mixtures, and how the efficiency of operation of commercial plants may be increased by proper partial condensation, especially in the case of alcohol-water. The design of total condensers is well understood, and standard textbooks such as Verdampfen, Kondensieren und Kühlen, by E. Hausbrand, contain sufficient data on cooling surfaces, radiation, heat transfers, etc., for their correct design and construction. But these same methods of design are usually employed in the case of partial condensers—in fact in commercial practice the same piece of apparatus is often used interchangeably as a partial or total condenser simply by regulating the flow of cooling water. It will be shown that in the case of the design of partial condensers several additional factors enter which have not heretofore been taken into account, and that in the great majority of cases the yield obtained from commercial apparatus, both partial condensers and rectifying columns, may be materially increased by proper condensation without increasing the coal consumption under the boilers.

If a mixture of two miscible liquids of different boiling points be boiled, the composition of the boiling liquid being kept constant, the vapor evolved will be richer in the more volatile constituent than the liquid, unless the latter be of the constant boiling composition, in which case the vapor is of the same composition as the liquid. The curves showing the composition of the liquid and the composition of the vapor in equilibrium with this liquid have been determined for many different mixtures, but for water-ethyl alcohol mixtures with which the experimental part of this paper is concerned, there are three (3) principal curves, as shown in Fig. 1; the Grönig, the Rachewsky, and the Sorel. The Grönig is the original data, but Sorel<sup>1</sup> claims that the composition of the vapor<sup>2</sup> in the upper part of Grönig's curve is greater than the true value, due to partial condensation of the vapor in the upper part of the distilling flask, and Sorel has accordingly applied

<sup>1</sup> *Compt. rend.*, 116, 693.



a correction to the Grönig data. The Rachewsky data seems to be a compromise between the Grönig and the Sorel. E. Hausbrand<sup>1</sup> states that the Sorel data is the most reliable, and that the condensation in practice, where there is always more or less priming, would be much closer to the Sorel curve than the Grönig. The Sorel data were used for all computations in this article where compositions of vapor-liquid are involved, for while they are not absolutely correct, yet they are the best at hand. It is desirable that the equilibrium liquid-vapor composition be known exactly<sup>2</sup> and that the necessary correction for priming be made for commercial cases.

In order that a vapor may be enriched in respect to the more volatile component, two general methods

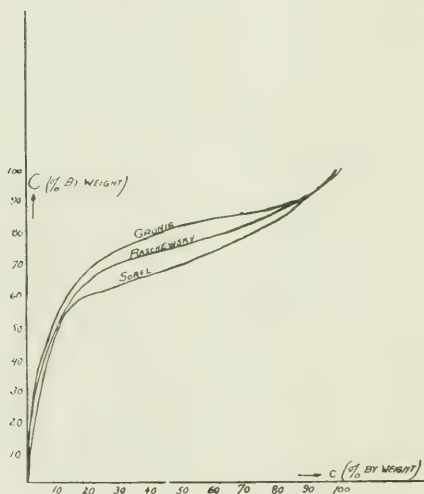


Fig. 1.

of procedure have long been in use. First, there may be induced a partial condensation in which a large portion of less volatile component and a smaller portion of the more volatile component may be deposited in liquid form, depending upon the removal of the latent heat by an external cooling medium, for example running water in a cooling coil. Second, the vapor may be enriched in respect to the more volatile constituent by rectification. This operation consists of an exchange of heat between vapor and liquid mixture only, the condensed vapor delivering its latent heat to the liquid, from which is vaporized in time a new vapor richer in the more volatile component. In order that the last operation may be

continuous each plate must have an appropriate intake and overflow of liquid from the plate above and to the plate below, respectively, the top plate being fed with the condensate from a partial or total condenser.

The nomenclature used in this article is as follows:

The composition of both vapor and liquid is expressed in per cent. by weight of the more volatile component—in the case of alcohol-water, by per cent. alcohol by weight. The composition of the vapor is expressed by  $C$ , with subscripts to denote the composition of different vapors such as  $C_1$ ,  $C_2$ , etc. The composition of the liquid is expressed by  $c$ , with subscripts to denote the composition of different liquids, such as  $c_1$ ,  $c_2$ , etc. Furthermore, the compositions of equilibrium vapor and liquid are denoted by the same subscripts, as  $C_1$ ,  $c_1$ ;  $C_2$ ,  $c_2$ ; the values to be found from Sorel's curve for each specific case. For weight of vapor two letters are used:  $G$  with proper subscripts such as  $G_1$  and  $G_2$  for the theoretical discussion, and  $W$  with proper subscripts, such as  $W_1$  and  $W_2$ , for actual experimental determinations. For instance, suppose that we wish to enrich a vapor of composition  $C_1$  to a vapor of composition  $C_2$  by partial condensation. By actual experiment a partial condensation is effected, and from a weight  $W_1$  of a vapor of composition  $C_1$  we have remaining a weight  $W_2$  of a vapor of composition  $C_2$ . The ratio  $W_2/W_1$  is called the yield. We can compute by use of the equations shown below the theoretical maximum yield that can be obtained in any given case. A weight  $G_1$  of vapor of composition  $C_1$  will give theoretically a maximum weight  $G_2$  of vapor of composition  $C_2$ .  $G_2/G_1$  is the theoretically maximum yield. Then  $W_2/W_1$ , the actual yield divided by  $G_2/G_1$ , the theoretical yield gives  $W_2G_1/W_1G_2$ , which, multiplied by 100, gives the percentage efficiency.

Since the total heat contained in the weight  $G_1$  of the vapor of composition  $C_1$  remains the same, however, the quantity  $G_2$  of the composition  $C_2$  varies, the percentage efficiency which here represents weight of product may be also taken as the thermal efficiency.

In a paper by Dr. W. K. Lewis,<sup>1</sup> of this laboratory, on "The Theory of Fractional Distillation," it was shown mathematically that the largest possible yield in enriching a vapor from a composition  $C_1$  to a composition  $C_2$  by partial condensation can be obtained when the conditions of a certain differential equation<sup>2</sup> are fulfilled, and such a condensation was accordingly

<sup>1</sup> THIS JOURNAL, 1, No. 8, 1909.

<sup>2</sup> If a weight  $G$  of vapor of composition  $C$  enter a partial condenser, and a weight  $dG$  is condensed, then,

$$\begin{aligned} C G &= (G - dG) C' dC + c dG \\ C G &= C G - C G dC - C dG + dG dC + c dG \\ dC C' &= G dC \\ dG G &= dC C' c \end{aligned}$$

$$\ln G_2/G_1 = \int_{C_1}^{C_2} \frac{dC}{C' C' c}$$

<sup>1</sup> E. Hausbrand, *Zett. f. Chem. Appar.*, 2, 585, 1907.

<sup>2</sup> A method for calculating exactly the composition of equilibrium vapor-liquid from thermodynamic data and from some of the laws of physical chemistry has been devised to check Sorel's curve. The results of this work will be presented in a later paper.

called a *differential one*. It was also shown that a differential condensation may be considered an infinite series of infinitesimal simple condensations, and is more efficient than a finite series of simple condensations between the same limits of composi-

tion change. The maximum theoretical yield may be computed for any given case graphically from the  $(C, 1/C - c)$  curve shown in Fig. 2, by planimentering the area under the curve between the limits of composition change, equating the value to the logarithmic



Fig. 2.

equation, and solving. The curves of maximum theoretical yield have been thus computed and are plotted in Fig. 10, so that by reference to these curves the maximum yield may be read off for any given practical case of composition change.

The two extremes of partial condensation are a simple condensation and a differential one, the former being the least efficient and the latter the most efficient. In the case of the enrichment of a vapor by simple condensation, the entering vapor (composition  $C_1$ ) is condensed to the extent that the condensate (composition  $c_2$ ) is in equilibrium with the final vapor (composition  $C_2$ ).

For example, suppose we wish to enrich a 35 per cent. vapor to one of 64 per cent. by one simple condensation, allowing the vapor to come to equilibrium with the resultant condensate. From Sorel's curve we find that the equilibrium liquid of a 64 per cent. vapor has a composition of 31.5 per cent. Assuming that we deal with 100 lbs. of entering vapor, then, 35 per cent.  $100 = 64$  per cent.  $X + 31.5$  per cent.  $(100 - X)$ .

$$X = 10.8 \text{ per cent.} = \text{yield.}$$

On the other hand, from an inspection of Fig. 10, showing the maximum yield theoretically obtainable by differential condensation, we find that in the enrichment of a vapor from 35 per cent. to 64 per cent. composition, the maximum yield is 45 per cent. These numerical examples show very clearly to how great an extent the yield depends upon the kind of condensation.

It was desirable first to determine experimentally how closely the differential or maximum yield could be approached. The efficiency obtained would thus indicate how near the actual partial condensation

very small amount at a time, and the process should be continuous.

(2) The condensate should be removed as fast as formed.

By fulfilling these conditions, there should be a number of very small simple condensations, and the yield of such a series should be much larger than in the case of a single simple condensation. When each

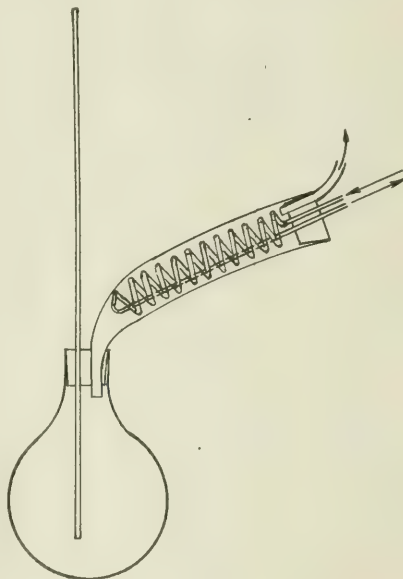


Fig. 4.

small amount of condensate has been deposited it is removed from the sphere of action for if it were allowed to remain, additional and undesired condensation would occur. Each small quantity of condensate should have a correspondingly small quantity of equilibrium vapor, but the condensate as a whole should not be in equilibrium with the uncondensed vapor; in fact the success with which this is prevented determines the efficiency of the partial condensation.

The first apparatus used is shown in Fig. 3. It consisted of a 5-liter R. B. flask and was heated in an oil bath which could be kept constant at any desired temperature. The condenser was of glass with a close-wound spiral through which the cooling water was circulated, the vapors passing around the spiral. The condensate was constantly siphoned off through a goose-neck. The uncondensed vapors from the partial condenser were passed into a total condenser which delivered the final product. The partial condenser, conducting tubes from the distilling flask and to the total condenser, the upper part of the distilling flask and the projecting ends of the spiral, were

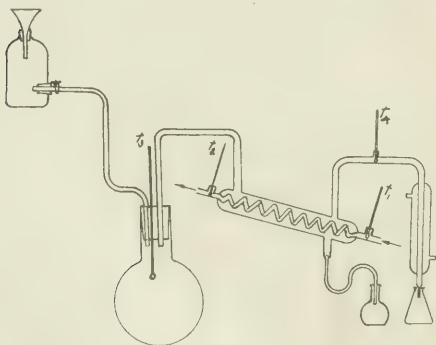


Fig. 3

was to the desired differential one. From the equations and the nature of the case, in building the first differential condenser the following conditions were fulfilled as nearly as possible:

(1) The vapor should be uniformly condensed, a



all thoroughly lagged with asbestos-magnesia insulating material. No recorded run was made before the apparatus was well warmed up, so that there was no appreciable condensation due to heat conduction from without during a run. The composition of the boiling liquid could be kept approximately constant by a return-feed of alcohol-water mixture. During a run the time was recorded in order to ascertain the rate at which the vapor was passed through the condenser. The samples were collected in tared flasks, the higher alcohol always in an Erlenmeyer, and the watery product in a F. B. flask. The increase in weight of the Erlenmeyer flask is  $W_2$  (composition  $C_2$ ), and the increase in weight of the F. B. flask added to  $W_2$  gives  $W_1$  the weight of the entering vapor (composition  $C_1$ ). The samples were analyzed by determining the specific gravity at constant temperature with a calibrated Westphal plummet with self-contained thermometer, a chemical balance sensitive to 1/10 mg. being used as the balancing medium. The composition determinations could be checked closely, and this method was found to be entirely satisfactory both as to speed and accuracy.

TABLE I.

Number of run	$t_1$	$t_2$	$t_3$	$t_4$	$C_1$ in per cent.	$C_2$ in per cent.	Rate of vapor.	Eff.
29 B	59.0	76.5	92.0	80.0+	49.5	74.5	13.2	17.7
30 B	59.0	76.5	92.5	81.0	48.2	69.3	16.9	47.5
31 B	59.0	77.0	92.3	85.0	48.1	68.7	21.5	77.8
32 B	59.0	77.5	92.5	85.5	46.8	67.3	22.5	77.4
33 B	59.0	78.0	92.5	86.5	45.0	63.8	24.6	83.5
34 B	59.0	76.0	92.5	86.0	42.9	63.7	24.1	84.5
35 B	59.0	76.0	92.0	85.0	47.1	66.4	24.8	84.8
36 B	59.0	76.5	92.0	86.0	45.3	63.6	27.5	88.9
37 B	59.0	76.0	93.0	82.8	41.7	67.9	14.5	33.8
38 B	59.0	76.5	93.0	84.0	41.0	64.3	15.8	40.6
39 B	59.0	76.0+92.0		85.6	48.4	66.6	28.0	90.8
40 B	59.0	76.5	93.0	87.5	46.9	61.8	37.8	95.0
41 B	59.0	83.0	92.5	85.0	43.4	66.8	22.7	77.5
42 B	59.0	85.0	92.5	85.5	46.0	66.1	24.8	91.4
43 B	59.0	85.0	92.0	85.5	47.4	65.5	29.5	92.2
25 A	52.0	69.0	91.5	82.0	49.0	71.5	21.4	35.0-
8 A	57.0	79.0	96.0	85.0+	25.0	65.5	12.9	50.0-
10 A	64.0	84.0	94.0+	89.0	39.4	57.3	15.0	87.0
11 A	59.5	84.0	94.0	89.0	36.4	58.5	13.8	71.6
22 A	59.0	77.0	92.5	85.0	47.0	65.5	26.4	87.0

$t_1$  = temp. of entering cooling water.

$t_2$  = " exit

$t_3$  = " entering vapor.

$t_4$  = " exit vapor.

Besides the preliminary series to determine the best method of manipulation, forty-three runs were made with the small apparatus and a number of these results are presented in Table I. An inspection of this table will show that in enriching a vapor from a low to a higher alcohol content the enrichment may be done with either a low or a high efficiency. A closer study will reveal that the efficiency depends upon the following factors: The rate of the passage of vapor must not be too low or otherwise a continuous and steady operation is impossible, and instead of differential there is apt to be only simple condensation in a portion of the apparatus. In the small laboratory apparatus used the minimum rate

for satisfactory operation proved to be about 25 cc./min. The temperatures of both the entering and the leaving cooling water is perhaps the most important factor in differential condensation. Suppose that a vapor entered the differential condenser at a temperature of 92° C. If the condensing surface at this end of the condenser is at a considerably lower temperature (say 20° less) it is easy to see that there will be a large condensation of vapor at this point. Not only must there be no material "jump" in temperature between the cooling surface and the entering vapor, but the same conditions must hold for the exit vapor and its cooling surface. In fact throughout the condenser, for an efficient condensation, the change in temperature of the vapor from its entrance to its exit must be uniform—theoretically it should be differential from point to point. The heat conductivity of glass being so small, the temperature on the outside of the glass spiral is considerably higher than the temperature of the cooling water at that point, and for this reason a metallic spiral should be used. Silver would be preferable, but copper or even tin serves this purpose very well.

An apparatus for laboratory use for the separation of miscible liquids by fractional distillation is sketched in Fig. 4. The condenser, which can be very easily and quickly, as well as cheaply, made, consists of an adapter tube with a small copper coil placed within. The copper return is covered with a glass tube to prevent condensation except along the surface of the spiral. The ordinary laboratory still-head, such as the Hempel, rod-and-disc, evaporator, etc., are fragile and expensive, and the enrichment of the vapor depends entirely upon condensation by air conduction (in some cases there is a very slight enrichment due to rectification). On account of the poor conductivity of glass the capacity is exceedingly small, the ordinary delivery of final condensate being about one drop per second. By using an adapter tube with copper spiral and regulating the temperature and rate of the entering cooling water to the proper values as explained above, 25 cc./min. or more of final distillate may be obtained with equally efficient separation.

The results with the small glass apparatus were so encouraging that it was decided to build a larger differential condenser and to try the idea on as large a scale as could be conveniently handled in this laboratory. The diagram of this differential condenser is shown in Fig. 5. The condenser consisted of a

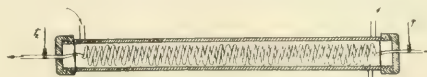


Fig. 5.

galvanized iron pipe, 3" inside diameter and 4 ft. long, with reducing caps, 3"-1", at the ends. The spiral

consisted of 20 feet of copper tubing  $1/4"$  o. d. No. 20 gauge, wound to fit inside the galvanized pipe. The condenser and all communicating tubes and pipes were heavily lagged with steam pipe insulation. In the first experiments the cooling water was circulated by gravity with a head of about  $8\frac{1}{2}$  feet, the water being heated by live steam in an elevated barrel of thirty gallons capacity. Even with suction the circulation was not as fast as was desired in some experiments, and so an iron tank of 60 gallons capacity was used as a reservoir, in which the water was heated by steam to the correct temperature, and by means of compressed air was circulated at the desired rate. In the later experiments an electrically driven gear pump was used and proved very satisfactory. A comparatively small amount of water could be used over and over, and the temperature was regulated simply by slightly cooling the exit water by radiation. By inserting resistance in the armature circuit of the motor, any desired rate could be had and maintained constant.

The still for supplying the vapors was of copper, 20 liter capacity with the bottom steam-jacketed. The still and entire steam system from calorimeter to exhaust was thoroughly insulated. However, when steam was used as a heating medium it was found impossible to maintain a constant rate of vapor even with a needle-valve adjustment and direct atmospheric exhaust, owing to the low quality of the steam and variations in the line pressure.

Electrical heating was finally resorted to and proved entirely satisfactory. An inexpensive heater of simple construction, which gave excellent service, consisted of ten arc-carbons, one-fourth inch diameter and about eleven inches long, mounted in two wooden rings (preferably white pine or cypress) o. d.  $7\frac{1}{2}"$ , i. d.  $4"$ . The carbons were connected in series by cast lead lugs, and the bottom was of wood which insulated the heater from the still, and was weighted with lead to keep it firmly seated. 25 amp. at 100 V. through this heater delivered over 75 cc./min. from 15 liters of a low alcohol.

With the single coil differential condenser 76 recorded runs were made and a number of different series are presented in Tables II and III. The amount of cooling water used was not measured in many of the early experiments, owing to the difficulty of accurately measuring it with the circulation system used at that time (gravity and suction). But in later experiments this was done and is discussed in detail further on.

Curves A and B shows the influence of temperature of the entering cooling water on the results obtained, and emphasize the effect of this temperature on the efficiency.

The great importance of having the temperature of the entering cooling water high enough was shown

TABLE II.

Number of run.	$t_1$ .	$t_2$	$t_3$	$t_4$	$C_1$	$C_2$ .	Rate <sup>1</sup> of vapor.	Eff.
10 C.....	63.0	89.0	93.0	88.5	53.4	62.4	92.0	73.7
12 C.....	60.0	91.0	93.0	88.0	47.1	60.0	114.5	51.8
13 C.....	55.0	90.0	93.0—	90.0+	41.8	51.0	200.0	65.4
14 C.....	72.5	90.0	94.0	90.5	39.5	52.0	90.0	74.5
15 C.....	58.0	90.0	94.0+	89.0	38.0	58.0	86.5	26.0
16 C.....	59.5	91.5	95.0+	88.5	37.0	58.0	90.0	13.8
18 C.....	69.0	92.0	95.5	89.5	34.0	50.2	46.0	50.7
19 C.....	61.0	91.5	95.5	91.5	34.0	49.0	77.5	46.0
20 C.....	74.0	90.0	95.0	86.0	36.8	66.8	50.0	73.3
21 C.....	76.0	91.0	95.0	90.0—	32.7	55.4	55.4	79.5
22 C.....	74.0	93.0	95.5	90.0+	33.0	51.0	55.7	52.0
23 C.....	75.0	91.5	95.5	89.5	30.7	55.4	53.0	75.5
24 C.....	75.0	92.0	95.5	90.0+	30.6	44.0	75.0	75.0
25 C.....	72.0	90.5	94.5	90.0	36.4	56.0	70.8	65.6
26 C.....	78.5	91.0	94.5	89.5	36.1	56.4	62.9	82.0
27 C.....	77.0	90.0	94.0	90.0	40.5	55.7	68.9	89.0
28 C.....	78.5	90.0	94.0+	89.5+	39.9	56.4	53.2	91.0
29 C.....	81.0	90.5	94.5	89.0	36.4	56.4	53.5	88.0
30 C.....	78.5	90.5	94.0+	89.0+	35.0	57.2	52.0	82.8
31 C.....	78.5	90.5	94.0—	90.0+	36.7	47.5	77.0	81.5
32 C.....	79.0	89.5	93.5	89.0	40.9	57.2	69.0	82.0
33 C.....	80.0	88.0	93.5	86.0	41.9	67.0	41.4	83.6
34 C.....	78.5	88.0	93.5	87.5	39.6	64.8	36.2	85.4
35 C.....	78.0—	89.0	93.5	87.5	41.7	62.8	57.8	71.0
36 C.....	80.0	90.5	94.0+	91.5	36.3	49.7	69.8	90.0
37 C.....	82.0	90.0—	94.0+	89.0—	37.9	60.5	35.6	85.5
38 C.....	79.5	90.5	94.0+	91.0	37.6	50.4	48.7	86.1
39 C.....	80.0	90.0	94.0—	87.5	38.7	64.0	40.6	82.7
40 C.....	78.5	90.5	94.0+	90.0+	36.1	53.4	59.4	81.7
41 C.....	78.5	90.5	94.0+	90.0+	34.9	56.3	35.8	79.0
42 C.....	80.5	90.0	94.0—	90.5	38.1	54.2	67.0	82.7
43 C.....	81.0	90.0	94.0+	90.5	36.5	54.7	40.4	81.6
44 C.....	81.5	84.5	89.0—	83.5	58.2	74.3	27.8	100.0
45 C.....	81.0	84.0	89.0	84.0—	57.3	73.9	32.5	100.0
46 C.....	79.0	86.0	94.0	82.0+	37.5	73.4	61.5	86.0
49 C.....	80.8	86.0	93.0	84.0—	45.5	70.1	53.5	92.8

TABLE III.

Number of run	$t_1$	$t_2$	$t_3$	$t_4$	$C_1$	$C_2$	Rate <sup>2</sup> of vapor.	C. W.	Eff.
1 E.....	74.5	79.0	81.3	79.0	76.0	83.3	50.6	2125	73.6
2 E.....	76.3	78.3	81.8	78.5	76.6	83.5	32.7	2000	57.7
3 E.....	76.4	78.4	81.5	78.0	75.7	83.6	24.4	1600	58.8
4 E.....	76.6	78.1	81.9	78.0	75.2	83.3	23.5	2280	37.1
5 E.....	75.6	79.0	81.5	79.2	76.8	81.4	32.4	1350	73.8
6 E.....	76.0	78.0	81.9	78.0	75.6	85.6	18.1	1275	57.0
7 E.....	76.5	78.1	82.0	78.0	77.0	84.5	19.7	1206	81.9
8 E.....	75.0	78.3	82.3	77.3	75.7	81.7	19.7	1000	38.9
9 E.....	75.0	78.6	82.8	78.0	75.7	84.2	46.6	274	45.5
10 E.....	77.8	78.0—	82.0	78.0+	79.0	85.8	23.4	3000	100.0
11 E.....	77.6	78.0	82.2	78.9	76.4	82.8	20.0	2980	62.2
12 E.....	77.8	78.0	81.8	79.0	77.3	83.4	17.0	2740	81.4
13 E.....	78.0	79.0	80.0		78.8	83.4	15.1	1830	87.6
14 E.....	77.5	78.0	81.4	78.0	71.7	82.5	15.2	2680	96.7
15 E.....	77.5	78.0	82.0	78.5	78.1	83.7	17.8	2625	100.0
16 E.....	77.5	78.0	82.0	79.0	76.5	82.8	17.5	2525	95.4
17 E.....	77.5	77.5	81.2	77.5	79.2	84.3	16.6	2675	90.0
18 E.....	77.5	77.5	81.2	78.5	79.4	83.3	19.2	2480	89.2
19 E.....	77.5	77.5	81.1	77.5	80.4	85.5	15.1	2200	65.0
20 E.....	77.9	78.0	81.0	78.5	80.0	84.4	12.6	2370	100.0
21 E.....	77.5	77.5	81.2	78.0	79.9	84.2	13.2	2525	90.8
22 E.....	77.0	77.0	80.3	78.0	79.9	84.3	10.5	2425	78.0
23 E.....	77.1	77.1	80.1	77.0	80.6	84.4	10.0	2375	85.6
24 E.....	76.9	77.0	80.2	78.0	79.6	84.3	10.5	2640	68.0
25 E.....	76.6	77.0	80.2	77.5	80.8	85.1	12.6	2725	70.0
26 E.....	76.4	77.0	80.1	76.5	80.0	85.6	10.9	1100	50.5
27 E.....	76.6	77.0—	79.9	77.8	81.8	85.5	19.2	1130	96.6
28 E.....	76.7	77.0	80.0	77.6	82.0	85.9	23.0	2630	100.0
29 E.....	76.5	77.0	79.8	75.0	81.2	85.5	10.5	1540	56.2
30 E.....	76.5	77.0	80.0	78.0	83.0	86.0	22.2	1260	100.0
31 E.....	76.5	77.0	80.0	78.0	80.9	86.3	20.5	1720	86.0
32 E.....	76.5	77.0	79.9	78.0	82.4	85.9	26.1	1175	48.5
33 E.....	76.5	77.5	80.1	78.0	81.9	85.9	23.1	1816	90.8
34 E.....	76.5	77.5	80.1	78.0	81.7	85.8	26.8	1725	98.5
35 E.....	76.0	77.0	80.1	76.7	80.9	89.1	18.3	1566	67.0
36 E.....	76.0	77.5	80.2	78.5	81.5	85.9	21.6	1320	83.1
37 E.....	76.0	77.5	80.3	78.0	81.8	85.4	21.4	1018	95.8

<sup>1</sup> Rate of vapor in cc. per minute.

<sup>2</sup> Rate of vapors and cooling water given in grams per minute.

recently by a case in commercial practice where cold water had previously been used in a partial condenser. When the temperature of the entering cooling water was raised and the amount properly regulated, the yield was double the best that had heretofore been obtained using cold water, and yet the enrichment of the vapors was the same in both cases.

The area of the cooling surface of the coil in the differential condenser was not as large as was desired, and it was feared that some of the vapors could probably pass through the space inside the coil at a high velocity without being properly enriched. Moreover, when the rate of vapor passage was rapid the air pressure required to supply the cooling water was so high that the rate of water circulation could not be kept constant. For these reasons a double coil was substituted for the single coil and was built as follows: A copper coil of the same length, diameter, and gauge as the original one was wound to fit within the first coil and the two coils were brazed together at each end. The second coil was wound left-handed with respect to the first, in order to hold it rigidly in place. The cooling water had two parallel paths of equal resistance to traverse, and thus with the same pressure heretofore used, twice the amount of water could be circulated. Baffle plates were placed within the inner coil to insure a thorough mixing up of vapors, and to prevent any vapor passing through the center of the condenser. The results obtained with this differential condenser are given in Table IV.:

TABLE IV.

Number of run.	$t_1$ .	$t_2$ .	$t_3$ .	$t_4$ .	$C_1$	$C_2$	Rate <sup>1</sup> of vapor.	Eff
1 F. . . .	77.3	81.5	88.0	81.3	57.4	77.2	58.5	100
2 F. . . .	78.5	81.5	88.0	81.8	57.7	75.9	55.0	100
3 F. . . .	79.2	82.3	88.5	82.5	58.3	74.4	52.9	100
4 F. . . .	79.0	83.0	91.5	81.0	47.5	77.9	34.4	100

The proper amount of cooling water to use in any differential condensation was determined in the following manner:

Suppose that a weight of vapor  $W_1$ , composition  $C_1$ , enters the differential condenser, is partially condensed, the uncondensed vapor having the weight  $W_2$ , composition  $C_2$ , and the condensate having the weight  $W_3$ , composition  $c_3$ .

We know that

$$W_1 = W_2 + W_3$$

and

$$C_1 W_1 = C_2 W_2 + c_3 W_3.$$

$L_1$  = total heat in vapor, composition  $C_1$ .

$L_2$  = total heat in vapor, composition  $C_2$ .

$H_3$  = heat in liquid, composition  $c_3$ .

$K$  = weight of cooling water.

The total heat must be equal to the sum of its components, and therefore for any case,

$$L_1 W_1 = L_2 W_2 + H_3 W_3 + K(t_2 - t_1).$$

The values for  $L$  and  $H$  are given in Hausbrand's article.<sup>1</sup> For any specific differential condensation, we have seen that the temperature  $t_1$  and  $t_2$  are fixed,  $t_2$  being slightly below the temperature of the entering vapor and  $t_1$  slightly below that of the exit vapor.

From the thermal equation given above it is seen that a certain definite quantity of heat,  $K(t_2 - t_1)$  per unit of time must be removed by the cooling water, and as the temperature change ( $t_2 - t_1$ ) is fixed, the amount of cooling water  $K$  must be a certain quantity, and can be calculated for each specific case.

In order to check this method the data from a very efficient run was used, and the calculation made as given below:

Rate = 44.5 grams = 0.098 lb. vapor per minute.

$C_1$  = 45 per cent.

$C_2$  = 74 per cent.

Rate cooling water = 5.5 lbs. per min.

$t_2 - t_1 = 9^\circ \text{F.}$

Maximum yield = 40 per cent.

$c_3$  = 25.7 per cent.

From tables (*l. c.*):

$L_1$  = 822 B. t. u.

$L_2$  = 628 B. t. u.

$H_3$  = 119 B. t. u.

Then,

$$0.098 \times 822 = (0.40 \times 0.098)628 + (0.60 \times 0.098)119 + (5.5 \times 9).$$

$$80.5 \text{ B. t. u.} = 24.6 + 7.0 + 49.5 \text{ B. t. u.} = 81.1$$

In some of the cases given in Table III the thermal equations will not check as closely as in the example given above, but these discrepancies are due to the fact that in series E the temperature differences of entering and exit cooling waters were very small and the temperature could not be read exactly because the thermometers were placed in oil wells. In the numerical example given above the temperature difference was large and therefore the percentage of error in determining  $t_2 - t_1$  was small.

In designing and building a differential condenser for commercial use the following method should be followed: The capacity of the condenser is known and the change in temperature of the cooling water is also approximately known for any change of composition of the vapors from  $C_1$  to  $C_2$ . It is known that the heat transfer must be made in a certain manner to obtain the maximum yield. From tables on the heat conductivity of copper the surface is calculated, and allowing for fairly close-coiling, and several coils being placed one within the other, the size of copper tubing to use is determined approximately. The size of tubes should be chosen of sufficient diameter to conduct easily the amount of cooling water necessary (see tables of flow of liquids through tubes). The weight of cooling water can be calculated as

<sup>1</sup> Rate of vapor in grams per minute

<sup>1</sup> *Loc. cit.*



shown above and if the apparatus is operated properly a high efficiency is assured.

A series of experiments were made to determine if the performance of the differential condenser is as efficient at high condensations as it is at low, and the results of this work are given in Table III. The apparatus is more difficult to regulate at the high concentrations, as each corresponding  $c$  and  $C$  lie closer together as the constant boiling mixture is approached and consequently the temperatures of the entering and exit cooling water must be delicately adjusted. In some cases a difference of a few tenths of a degree in the temperature of the entering cooling water materially affected the efficiency in that particular run. Fluctuations in temperature, rate of cooling water or vapor that would not be noticed at low concentrations were troublesome at high. An apparatus in which a composition change of 40 per cent.

enrich the vapors from about 25 per cent. to 75 per cent., can be built and run at a high efficiency, but for higher alcohols the differential condenser cannot be so conveniently used for reasons given above. As the high proof of the rectified alcohol is of first importance to many distillers, it was desired to be able to produce as high a proof as was wanted at a high efficiency of operation.

An efficiency test on one of the very latest types of French distilling apparatus was made by the writer, and the thermal efficiency of the rectifying column alone was computed as 40 per cent. of the theoretical maximum, which is high for the average column. The composition of liquid and vapor in different parts of the apparatus was as follows:

Composition of final distillate, 193° (96.5 per cent. by vol.).
Composition of vapors entering bottom plate, $C_0 = 20.6$ per cent.
Composition of vapors entering second plate, $C_1 = 58.5$ per cent.
Composition of vapors entering third plate, $C_2 = 68.0$ per cent.
Composition of liquid on the bottom plate, $c_1 = 14.2$ per cent.
Composition of liquid on the second plate, $c_2 = 43.2$ per cent.

This test showed that the composition change on the bottom plates was very rapid, and as the change from successive plate to plate is done by simple rectification, the yield in this part of the apparatus was poor. The column tested had eighty-eight plates, of which the greater number were used for rectification of high vapors.

The ordinary type of rectifier column can be more efficiently operated if the apparatus is well insulated and if the composition change from plate to plate is small. Ordinarily, this latter would mean that an apparatus twice the size of the one in use for the same composition change and the same capacity would be required, and on account of cost of installation this is prohibitive. Many designers have tried to build apparatus having large capacity and a small number of plates, and the operation depended upon the rapid enrichment of the vapors in the bottom plate. Although the first cost is reduced, it is impossible to obtain a high efficiency with such an apparatus because the total rectification is a series of simple rectifications of large composition change, and the yield is therefore low. In case it is desired to obtain high proof, the last step in concentration can most successfully be accomplished by using a plate column. Above this a total condenser, returning the calculated amount of overflow from the same to the top plate, will usually be found most satisfactory, requiring much less attention at this high proof and yielding results almost as economical as a differential type. This is due to the fact that the composition of vapor and liquid at these high proofs lie so close together. A differential condenser is not suitable for the last step in concentration for high alcohols but can be most successfully used during the earlier steps of rectification.

Fig. 6 is a sketch of a plate column of eight plates

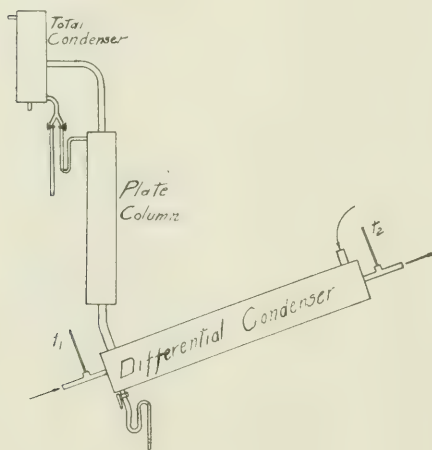


Fig. 6

can be easily effected at low concentrations may only be large enough to give a composition change of 10 per cent. or less at high concentrations. So if a 190° proof alcohol is desired, the size of the differential condenser may be several times as large as that necessary if only 145° proof alcohol is required, if the passage of the vapor be rapid. Except for the susceptibility of the apparatus to slight changes of temperature and rate, and the increased size of apparatus necessary if the output is large, it is not especially difficult to obtain a high alcohol at a high efficiency by differential condensation. With the single coil apparatus a 186° proof alcohol at approximately 100 per cent. efficiency was obtained.

A differential condenser of medium size (compared with the size of the ordinary dealcoholating and rectifying columns) and large capacity, which will

delivering into a total condenser with return-feed to the top plate, the rectifying column being placed above a differential condenser. The proper return-feed from the total condenser is calculated as follows:

It has been shown<sup>1</sup> that a rectifying column is working at its maximum efficiency when the composition of the overflow from the bottom plate is equal to that of the equilibrium liquid of the vapor entering the bottom plate. If the composition of the entering vapor is  $C_o$ , that of the rectified vapor  $C_c$ , then for  $W_o$  pounds of entering vapor the maximum yield of final product  $W_c$  is given by the equation

$$\frac{W_c}{W_o} = \frac{C_o - c_o}{C_c - c_o}$$

The total weight of alcohol mixture of composition  $C_c$  that can be obtained from the weight of entering

ted under conditions which previous tests had shown allowed a very high efficiency to be obtained.

Forty and five-tenths per cent. of the vapors condensed in the total condenser were returned to the

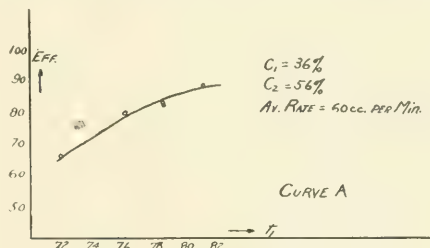


Fig. 8.

top plate. The theoretical amount to be returned for a composition change from 74 per cent. to 85.3 per cent. was 38.8 per cent., calculated from the formula:

$$\text{Max. yield (for plate columns)} = \frac{C_o - c_o}{C_c - c_o}$$

The actual yield of final product was 22.86 grams in  $2\frac{1}{2}$  min.; 111.35 grams of 45.1 per cent. vapor entered the condenser, and the maximum yield (40 per cent. of the weight of entering vapor) = 44.56 grams of 74 per cent. vapor entered the plate column, and was enriched to 85.3 per cent. in that space of time ( $2\frac{1}{2}$  min.).

The maximum yield of the final product was:

$$W_c = W_o \frac{C_o - c_o}{C_c - c_o} = 44.56 \frac{0.74 - 0.59}{0.853 - 0.59} = 44.56 \times 0.57 = 25.4 \text{ gm.}$$

The yield obtained was 22.86 grams.

$$\text{Efficiency of total operation} = \frac{22.86}{25.7} = 90.2 \text{ per cent.}$$

The apparatus was run in this manner for several consecutive days for about 10 hours daily, and the performance was perfectly steady and constant at all times. The plate column used had only eight plates,

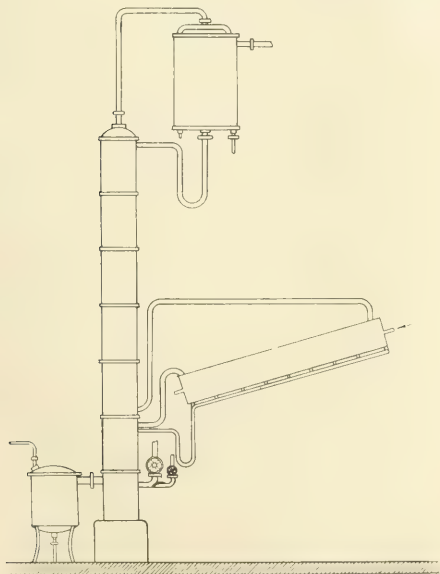


Fig. 7.

vapor  $W_o$ , composition  $C_o$  is calculated, and after subtracting the maximum yield  $W_c$  the remainder gives the amount of distillate of composition  $C_c$  that should be returned to the top plate of the plate column.

The results of a test with the apparatus of Fig. 6 are as follows:

Composition of vapors entering diff. cond. = 45.1 per cent.  
Rate of vapors entering diff. cond. = 44.5 gram./min.  
Composition of vapors leaving diff. cond. = 74.0 per cent.  
Composition of final product from plate column = 85.3 per cent. (by vol. 90 per cent.).

The double coil differential condenser was opera-

Levis, Loc. cit.

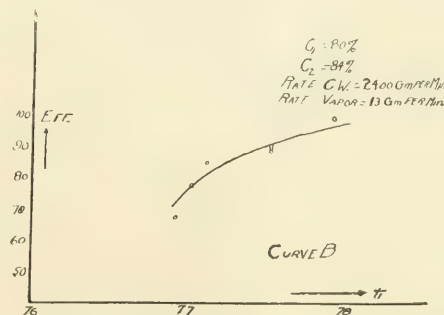


Fig. 9.

but if enough plates are used, and this method carefully followed, an alcohol approaching the composition of the constant boiling mixture can be obtained. The apparatus as run in the above test corresponded

apparatus being 90 per cent. of the theoretical maximum.

It was shown<sup>1</sup> that a differential condenser placed above a plate column and returning the differential

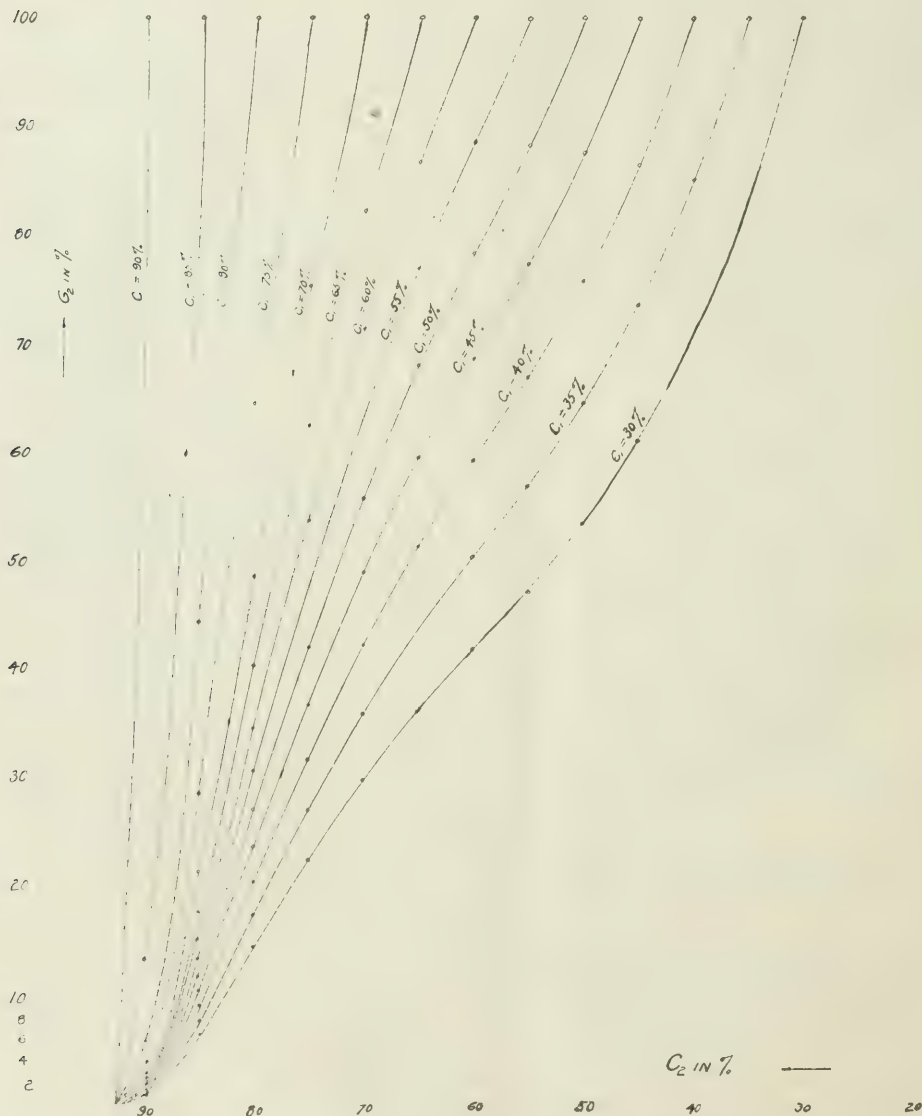


Fig. 10.

to a continuous distillation and rectification apparatus using a 14 per cent. (by vol.) mash and delivering a 90 per cent. (by vol.) alcohol, the performance of the

condensate to the top plate reduces the number of plates necessary to a minimum and enables the

<sup>1</sup> Lewis, *Loc. cit.*



operation of the plate column to be made at a high efficiency. The condensate from a differential condenser should never be returned directly to the still, but should always be passed through a short plate column which removes the maximum amount of the volatile component from the condensate, and the overflow from the bottom plates is of approximately the same composition as the liquid in the still—the condition of maximum efficiency.

Fig. 7 shows the arrangement which should be used to increase the efficiency of commercial rectifying columns. The rectifying column is made into two columns, the lower one being rather short, by placing a solid metal sheet between two successive plates. The lower column should contain fifteen or twenty plates,<sup>1</sup> and the vapors from the top plate of this short column should pass into the differential condenser,<sup>2</sup> and after being properly enriched (a composition change of 50 or 60 per cent.) should then pass into the upper plate column for rectification for proof. The vapors from the top plate of the upper column should pass into a total condenser and the calculated amount returned to the top plate. The overflow from the bottom plate of the upper column should pass into the top plate of the lower column, and if the whole apparatus is well lagged, a high efficiency is easy of attainment. In case high proof (above 85 per cent. by volume) is not required, the upper column may be omitted.

The differential condenser is simply and cheaply built, the proper design of the coil being most important. The cooling water is used continuously, and some method of initially heating it to the proper temperature, either with live steam or coils, should be used. The circulation may be accomplished by either a force or gear pump, or in some cases gravity flow might give the volume required. The exit cooling water may be cooled down to the proper intake temperature by spray or by flow over baffle plates.

#### CONCLUSION.

An apparatus has been developed for partial condensation of mixed vapors, to be used in conjunction with a plate rectifying column below it, and if necessary with a further column above it, which will:

(1) Materially increase the thermal efficiency and capacity of commercial types of rectifying apparatus, and

(2) Decrease the initial cost of the same by decreasing the length of the plate towers used.

Extensive experimental results have been submitted to prove the accuracy of the deductions and conclusions, and to furnish data for the proper design

<sup>1</sup> The correct methods of design for such a column can be found in Lewis' article.

<sup>2</sup> It will be noticed that in Fig. 7 the differential condenser is tipped so that the condensate flows towards the entering vapor. This is for the purpose of preventing any depletion whatever of the vapor in volatile component, although the condensate is removed as fast as formed from the sphere of action by tubes shown in the sketch.

of such apparatus; the methods and calculations for such designs have been outlined.

### CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM, AND THE DETECTION OF CAPSICUM.

By E. K. NELSON.

Received August 1, 1910.

Thresh,<sup>1</sup> in 1876, established the fact that a crystalline, powerfully pungent principle, which he named capsaisin, is the main active body in capsicum.

Morbitz<sup>2</sup> isolated a principle from capsicum which he termed "capsacutin," but Micko,<sup>3</sup> who has done the most recent work on the subject, showed that the body isolated by Morbitz is identical with the capsaisin of Thresh, being probably an impure form of the latter body.

Micko developed a process for the isolation of capsaisin and proved it to be the pungent principle of pepper (*capsicum fastigiatum*), but that *capsicum fastigiatum* contains about twenty times as much capsaisin as does *capsicum annuum*.<sup>4</sup>

In view of the fact that the detection of capsicum is desirable in those cases where it is used to fortify pungent beverages, such as ginger ale, it seemed desirable to isolate some of the pure principle for the purpose of studying some of its properties.

The method of Micko was employed, and while extremely tedious and difficult, it is apparently the only way at present known whereby the body can be satisfactorily separated from the fatty and resinous bodies with which it is associated.

Fifteen hundred grams of ground African cayenne were completely exhausted with ether. The ether was distilled off and the residue, a red, very pungent oil, was dissolved in 1 liter of 90 per cent. alcohol, made slightly alkaline with alcoholic potash, and well agitated. A portion of the oil remained undissolved. This was separated, agitated with 90 per cent. alcohol, and the alcoholic solutions, which contained the pungent principle, were united. Barium chlorid solution was added to the alcoholic solution in moderate excess and the mixture was thoroughly agitated. After standing for several hours, the clear liquid was decanted from the precipitate and the latter was washed with alcohol on a glass wool filter.

The alcohol from the alcoholic solution was removed by distillation, and the residue was agitated with warm water. On standing, an oil separated, which was removed and the aqueous layer was shaken out with chloroform, the residue from which was united with the main portion of oil. The oil was taken up with 90 per cent. alcohol, exactly neutralized with alcoholic potash, and sufficient alcohol added to bring

<sup>1</sup> *Phar. Jour. and Trans.*, **3**, 7, 21, 259, 473.

<sup>2</sup> *Phar. Zeitsch. f. Russland*, **1897**, 369.

<sup>3</sup> *Zeits. f. Unters. d. N. u. Genussm.*, **1898**, 818.

<sup>4</sup> *Ibid.*, **1899**, 411.

the volume to two liters. Alcoholic solution of silver nitrate was then added, while stirring, in moderate excess. A brownish red, very voluminous precipitate was thrown down which was filtered off and washed with alcohol until the pungent principle was completely removed.

From the filtrate silver nitrate was removed by adding sodium chlorid in aqueous solution, and filtering. The alcohol was distilled from the filtrate, the residue mixed with water and the oil separated. This oily material was then dissolved with an excess of five per cent. potassium hydrate solution and carbon dioxid passed into the solution until it was completely saturated with that gas.

This caused the separation of an oily layer which was removed by shaking out with ether. The residue from the ether was put into an eight-liter flask, mixed with 100 cc. of five per cent. potassium hydrate, diluted with three liters of water, heated to 60°, and allowed to stand overnight at room temperature. The alkaline, slightly colored, clear solution was siphoned from the oily, insoluble material left adhering to the walls of the flask.

The above process was repeated until pungent bodies were completely removed from the residue. The alkaline, clear solutions thus obtained were united in a large flask, heated to 60° and barium chlorid solution, in sufficient excess, was added, while stirring.

On standing, the precipitate settled out and the clear, supernatant liquor was removed. The precipitate was repeatedly treated with dilute potassium hydrate solution and subsequent precipitation with barium chloride until it was free from pungent bodies. The clear, filtered solutions from the barium precipitate were acidified (whereupon they became milky), and shaken out with chloroform.

The chloroform was evaporated and after standing for some days the residue began to crystallize in rosettes and set finally to a solid, beautifully crystalline mass. The crystalline material had a brownish yellow color and was contaminated with some oily material. It was spread on a porous plate and the oil and much of the color absorbed. The crude crystals were dissolved in carbon bisulphid, a gummy residue remaining undissolved.

The carbon bisulphid was evaporated in a flask and the residue boiled out with petroleum ether under a reflux condenser, decanting the petroleum ether extracts into beakers.

Upon cooling, pearly leaflets separated from the petroleum ether solutions.

The body thus obtained was perfectly pure capsaicin, in the form of pearly white leaflets.

All residues and liquors were carefully examined for other bodies of a pungent nature with negative results. Hence, it is concluded that capsaicin is the only pungent principle of capsicum. An alkaloidal

substance, capsaicin, possessing a conin-like odor, is present in minute amount, but it is not pungent.

From 1500 grams of selected African pods (capsicum fastigiatum), 2.13 grams of pure, crystalline capsaicin were obtained, representing 0.14 per cent. of the original material. The crystals melt at 64.5° (Micko's capsaicin melted at 64°). The properties of the body agree well with those described by Micko.

Capsaicin is not an alkaloidal body but possesses some of the properties of the phenol group. Micko has shown that it contains a methoxy group and a hydroxyl group and from analysis and molecular weight determinations ascribes to it the formula  $C_{18}H_{28}NO_3$ . The enormous pungency of capsaicin can be appreciated only by those who have been brought intimately in contact with it. One drop of a solution containing 1 part in 100,000 causes a persistent burning on the tongue. A drop of a solution of 1 part to a million imparts a perceptible warmth.

Now one drop of a solution of one part per million contains at the most 1/20,000 of a milligram of capsaicin, an amount not only unweighable, but extremely difficult of detection even by the most delicate of chemical reagents. The only test based on chemical reaction indicating capsaicin on record, to the writer's knowledge, is that described by Micko,<sup>1</sup> and is as follows: An alcoholic solution of capsaicin acidulated with hydrochloric acid is treated with an excess of platinic chlorid; no precipitate is formed. On spontaneous evaporation of this mixture, however, a characteristic vanilla-like odor is developed after some time.

To test the delicacy of this reaction, weighed amounts of capsaicin in alcoholic solution were treated with platinic chlorid and hydrochloric acid, as directed, with the following results:

- 4 10 mg. gave no odor.
- 2 mg. gave a slight odor which could not be described as the odor of vanilla.
- 4 mg. gave a slight vanilla odor.
- 10 mg. gave a distinct vanilla odor.

Thus it seems that this method, depending on the sense of smell, is entirely valueless for the detection of small amounts of capsicum. Careful search was made for a microchemical reaction which could be utilized for the detection of small amounts of capsaicin, but none was found.

The following test indicates the presence of capsaicin: On treating a small amount of capsaicin with a dilute neutral solution of ferric chloride and a little alcohol, an evanescent greenish blue color is given. This reaction is neither characteristic nor delicate, and is therefore of no value for analytical purposes.

When capsaicin is dissolved in sulphuric acid and a particle of sugar added, a beautiful violet color de-

<sup>1</sup> *Zeits. f. Unters. d. Nahr. u. Genussm.*, 1898, 818.

velops on standing, a reaction, however, which is afforded by other substances.

The detection of small amounts of capsicum therefore appears to be restricted to the physiological action of the capsacin.

Garnett and Grier<sup>1</sup> were the first to describe a method for the detection of capsicum in ginger preparations, based on this reaction. The pungent body of ginger (gingerol) is destroyed by them by heating on the water bath with alcohol potassium hydrate.

The pungent substance of ginger is not, however, completely destroyed by this method, as can readily be observed by the very perceptible burning taste left after treating tincture of ginger by their method. Furthermore, the residue obtained according to this method is quite considerable, as ether is used for the extraction, and it dissolves the "oleo-resins of ginger, thus diluting the pungent body in the residue and rendering the test less delicate.

A method is here proposed which departs from the Garnett and Grier method in important particulars and which is described as follows:

Ten cc. of a tincture, or the ether extract from 100 cc. of a beverage (from which any alcohol present has been evaporated previous to extraction with ether) are treated in a porcelain dish with 10 cc. double normal alcoholic potassium hydroxide and evaporated on the steam bath.

About  $\frac{1}{10}$  grain powdered manganese dioxid is added, 5-10 cc. water, and the heating on the bath continued for about 20 minutes, or until volatile oils are expelled. Cool, acidify with dilute sulphuric acid and extract at once with petroleum ether. Evaporate the petroleum ether in a small crucible, keeping the residue within as small an area as possible and heating on the steam bath for about five minutes. The residue will be very small and in some cases scarcely visible, and it will contain all the capsacin from capsicum, mixed with a minimum amount of extractive matter. Apply the tongue to the residue, being careful to keep the material on the tip of the tongue. If capsicum is present the characteristic burning sensation will soon be felt.

If a minute amount of capsicum is present, it may take a few minutes for the reaction to develop. In some cases it may be necessary to apply the entire residue to the tongue.

From the nature of the substance it is desirable to allow an interval of time between the several testings. Failure to follow this course may result in confusion.

The following data will show the delicacy of the test where capsicum in small amount is mixed with ginger:

Tr. ginger	U. S. P.	10 cc.	} No capsicum found.
Tr. capsicum	U. S. P.	none	
Tr. ginger	U. S. P.	10 cc.	} Capsicum detected by placing entire residue on tongue.
Tr. capsicum	U. S. P.	1, 100 cc.	
Tr. ginger	U. S. P.	10 cc.	} Capsicum taste very pronounced.
Tr. capsicum	U. S. P.	1/10 cc.	
Tr. ginger	U. S. P.	10 cc.	} Capsicum taste, extremely hot.
Tr. capsicum	U. S. P.	5/10 cc.	

BUREAU OF CHEMISTRY,  
WASHINGTON, D. C.

## ASAFETIDA.

By W. A. PEARSON.

Received August 1, 1910.

During the past few years so much analytical data has been presented on this subject that I hesitate to increase the voluminous records. However, after the unpleasant and tedious work has been accomplished it affords some relief to give others what little benefit may be derived from it.

When the Federal law first took effect there was a marked and prompt improvement in the quality of consignments of asafetida, but after a few inferior lots had failed to be deported the European merchants were quick to declare that the highest grades could not be obtained in sufficient quantities. Possibly the ultimate motive for this attitude was to influence the Revision Committee of the Pharmacopeia to adopt lower standards.

*The Great Variation Due to Sampling of Gum Asafetida.*—Every one is acquainted with the difficulty of obtaining representative samples of gum asafetida. An actual illustration may well be given.

A sample consisting of several lumps was pounded in an iron mortar till fairly uniform and the ash amounted to 24.9 per cent., the alcohol-soluble 50.86 per cent. The same case was later resampled and the average of four results obtained indicated 54.5 per cent. of ash and only 23.2 per cent. of alcohol-soluble material, almost the reverse of the results formerly obtained.

Samples from other cases in the same lot contained 27.6 per cent. alcohol-soluble, 50.9 per cent. ash, 27.5 per cent. alcohol-soluble and 52.9 per cent. of ash.

*Collection of Samples.*—An attempt was made to get representative samples by taking portions of several lumps from each case. If the total sample was much over one pound, half of each piece sent for examination was taken. The samples were always pounded in an iron mortar until the material could be mixed with the hands and was of fairly uniform consistency. The degree of variation obtained with this material by two chemists can be seen from the following table:

<sup>1</sup> *Pharm. Jour. and Trans.* (3), 12, 721.



## PER CENT. OF ASH.

Sample No. 1		Chemist.
	Per cent.	
Determination No. 1.....	58.8	H. M. S.
Determination No. 2.....	51.1	H. M. S.
Determination No. 3.....	55.4	W. A. P.
Determination No. 4.....	52.5	W. A. P.

Average..... 54.5

## Sample No. 2.

Determination No. 1.....	52.5	H. M. S.
Determination No. 2.....	51.1	H. M. S.
Determination No. 3.....	52.0	W. A. P.
Determination No. 4.....	47.8	W. A. P.

Average..... 50.9

## Sample No. 3.

Determination No. 1.....	53.3	H. M. S.
Determination No. 2.....	54.4	H. M. S.
Determination No. 3.....	54.7	W. A. P.
Determination No. 4.....	49.4	W. A. P.

Average..... 52.9

## AMOUNT OF ALCOHOL-SOLUBLE MATERIAL

## Sample No. 1

	Per cent.	Chemist.
Determination No. 1.....	20.3	H. M. S.
Determination No. 2.....	24.2	H. M. S.
Determination No. 3.....	25.6	W. A. P.
Determination No. 4.....	22.8	W. A. P.

Average..... 23.2

## Sample No. 2.

Determination No. 1.....	28.0	H. M. S.
Determination No. 2.....	29.0	H. M. S.
Determination No. 3.....	27.3	W. A. P.
Determination No. 4.....	26.1	W. A. P.

Average..... 27.6

## Sample No. 3.

Determination No. 1.....	29.4	H. M. S.
Determination No. 2.....	27.5	H. M. S.
Determination No. 3.....	26.1	W. A. P.
Determination No. 4.....	26.0	W. A. P.

Average..... 27.3

*Method of Determining Per Cent. of Alcohol-soluble Material.*—The amount of alcohol-soluble material was determined by shaking about ten grams of the sample with 150 cc. of alcohol in a mechanical shaker for several hours. The insoluble material was collected on tared filter paper and well washed with an excess of alcohol before drying to a constant weight at 100° C. It has been suggested that this residue be taken after weighing for the determination of ash, but several obvious reasons make this method objectionable.

The results given above were obtained in the usual routine examinations and show the extent of the variations that may be expected.

*Powdered Asafetida.*—Powdered asafetida theoretically should conform to the same standards as the gum asafetida, but every one who has attempted to powder it knows that it is not convenient to reach these standards on account of the moisture and volatile matter that is present. If it is dried before powdering, considerable of the volatile material is lost.

The following records given by Mr. F. P. Sher show the loss of asafetida during drying and powdering:

Lot No. 1, 2032 lbs	Returned after powdering, 1630 lbs.	Loss, 402 lbs.
Lot No. 2, 1055 lbs	Returned after powdering, 844 lbs.	Loss, 211 lbs.
Lot No. 3, 515 lbs.	Returned after powdering, 448 lbs.	Loss, 267 lbs.
Lot No. 4, 936 lbs	Returned after powdering, 697 lbs.	Loss, 239 lbs.
Total.....	4538 lbs	3619 lbs. 1119 lbs.

The average loss in drying is 24.6 per cent., and this loss is almost entirely the volatile and alcohol-soluble portion, which loss indirectly increases the ash and alcohol-insoluble material in the finished product.

For example, if 100 lbs. of asafetida containing 50 per cent. insoluble material and containing 15 per cent. of ash, be powdered and lose 20 per cent. in powdering, the resulting 80 lbs. of powder will still contain 50 lbs. of insoluble material, or 60.2 per cent., and it will still contain 15 lbs. of ash, or 18.7 per cent.

It can be easily seen that powdered asafetida contains considerably more ash and considerably less soluble matter. The analytical results on powdered samples will not vary nearly as much as on the samples of gum, because of its comparative uniformity.

The following data illustrates the variation obtained in determining the per cent. insoluble in alcohol of the powdered asafetida:

## INSOLUBLE IN ALCOHOL.

## Lot No. 1.

	Per cent.
Determination No. 1.....	59.00
Determination No. 2.....	58.84
Determination No. 3.....	59.26
Determination No. 4.....	58.88
Average.....	58.99

## Lot No. 2.

Determination No. 1.....	51.40
Determination No. 2.....	52.92
Average.....	52.16

## Lot No. 3.

Determination No. 1.....	83.08
Determination No. 2.....	82.52
Average.....	82.80

*Ash Determinations.*—It is frequently noticed in making ash determinations that lower results are obtained by using a blast lamp and also if the length of time ash is heated is increased. It is not wise to take a very small sample, particularly of the gum for ash determination, because the presence or absence of a single small stone will make the results widely divergent. On the other hand, a large amount of ash requires a great amount of heat and must be heated a long time before it becomes perfectly white.

To ascertain the amount of variation due to method of heating, the following ash determinations were made upon three samples of powdered asafetida:

Sample No. 1.	Sample No. 2.	Sample No. 3.
Per cent.	Per cent.	Per cent.
Determination No. 1.... 36.11	29.25	46.3
Determination No. 2.... 32.08	28.20	45.1

The first determinations were made by heating

about ten grams in a platinum dish over a Bunsen burner for five hours. The second determinations were made by heating about ten grams in a nickel crucible for fifteen minutes with a blast lamp.

The above data are presented not only to show the variations due to sampling and assaying, but also to give the retail pharmacist some reason for the lack of uniformity of his tincture of asafetida. Perhaps the present method of valuation is far from ideal, but certainly some definite standard for the amount of soluble constituents in the tincture should be insisted upon.

Acknowledgment are due Mr. H. M. Sechler for considerable amount of the data here presented.

ANALYTICAL DEPARTMENT.  
SMITH, KLINE & FRENCH CO.

## ADDRESSES.

### CHEMISTRY IN THE BUREAU OF STANDARDS.

By W. F. HILLEBRAND, Chief Chemist.

Received September 7, 1910.

I have felt impelled to speak on the subject "Chemistry in the Bureau of Standards," for the reason, mainly, that since my connection with that bureau little published evidence of chemical activity has been offered. The impression might arise and spread that proper advantage is not taken of the opportunities provided. It is my wish to forestall such an opinion. That the public closely interested in chemistry has a right to be informed on the subject goes without saying, for the bureau is a federal institution where work is expected to be directed chiefly toward providing the public with authentic information on a variety of subjects. This information must be of value for the most part to the industries, otherwise the bureau fails in its chief function. From its inception the bureau has endeavored to meet the most insistent demands upon its reservoir of physical knowledge, and at an increasing rate as facilities were given it for so doing. That it has been in the main eminently successful in this respect, is sufficiently attested by the support it has at all times received from Congress and by the marked growth it has experienced and is experiencing, a growth that would be impossible without strong backing, that is, the approval of an influential section of the community both industrial and educational, manifested through its representatives in the national capitol.

The growth of the chemical side of the bureau has been slow, but it is now increasing rapidly at a rate which bids fair to call for a special building within a couple of years. At the start it was not clear, apparently, along what lines the chemical work of the bureau might best develop and I was myself in doubt for some time. The viewpoint of my predecessor, Dr. Noyes, that research without direct practical bearing should not be elbowed out of view by the demands of the industries, is one that should need no defense before a gathering of this character. It is a view that is held by the director of the bureau as well as by myself. Nevertheless, during the interval between the withdrawal of Dr. Noyes from the bureau and my own transfer to it, the work of the small chemical force was wholly along practical lines. The demands of one and another of the government bureaus and departments for help in the preparation of specifications for materials in which they were vitally interested had become insistent. Dr. Stokes, the associate chemist in charge, was deeply impressed with the importance of the numerous problems presented and devoted himself with ardor and great ability to their solution.

He had mapped out extensive lines of investigation and had initiated several different researches of a most difficult nature. Unfortunately, his withdrawal from the bureau has hindered the prosecution of some of this work for lack of a directing spirit with full comprehension of the subject in its different bearings. At the same time it was felt, in view of the obscurity in which some of the questions were involved and the length of time needed for their study and the uncertainty of a successful issue, that our chief attention should be centered for the present on other lines of work where success was practically assured and the immediate value to the community was plainly evident.

The most important of these problems was a great extension of one already initiated under Dr. Noyes, namely, the providing of carefully analyzed materials by which chemists can check the accuracy of their analytical methods and employers can control the work of their employees. The usefulness of these materials is not confined to those employed in the industries but extends equally to educational institutions. To you, being chemists, it is hardly necessary to offer any arguments in support of the use of such standardized materials. The subject is treated briefly, but with sufficient fullness, in a publication which has been issued only very recently as a circular of information regarding the samples that have been provided thus far by the bureau or are in immediate preparation, some thirty-seven in all. The number will be very largely added to, for there is an ever increasing demand in this direction, and I feel that the bureau can do no greater service to chemists of the industries at present than by catering to this demand. Not only will benefit result from the use of the samples themselves but also from the experience that the bureau chemists will gain, and have already gained, in their close study of the methods employed in analyzing them. To this feature I will revert later.

The list of samples in stock comprises three pig irons, 5 Bessemer steels, 5 basic open-hearth steels, 6 acid open-hearth steels, and 1 vanadium steel, to which will be added, as soon as analysis can be made, a nickel steel, a chrome-vanadium steel, and a chrome-tungsten steel. Of ores there are an argillaceous limestone, suitable for the manufacture of Portland cement, a zinc ore, and 3 iron ores from the Lake Superior region. It is impossible to find any single ore from this region that can advantageously be used as a standard for all the constituents that are ordinarily determined in an iron ore. Hence, the multiplication, one being used for iron, phosphorus and silica, the second for alumina, lime and magnesia, and the third for manganese. A titaniferous iron ore from New Jersey is in process of analysis, and it is proposed to provide later one typical ore from the Alabama region. Possibly typical ores of lead and zinc from the Rocky Mountain region will follow.

It is to be said here, however, that the selection of ores that can be used advantageously as standards for analysis offers far greater difficulty than that of alloys, for the reason that they are almost always so subject to changes in moisture content from day to day or at different altitudes, as to detract very much from their value. If their sensitiveness to hygro-metric variations is at all pronounced it is almost hopeless to expect that all chemists will be able to reduce them to a fixed water content, no matter how precisely formulated may be the directions for drying. The moisture content may vary somewhat without detriment so far as the minor constituents are concerned, but not so for those present in large amounts.

We have also a pure sugar for use as a standard in calorimetric and saccharimetric work, and studies are in progress looking to the applicability of other standards for the measurement of heat of combustion, such as benzoic, salicylic, phthalic and hippuric acids, naphthalene, anthracene and camphor. This work is done in co-operation with the heat division of the bureau.

The American Brass Foundrymen's Association has enlisted our aid in the preparation of standard brasses and bronzes, and a beginning has been made with two brasses, which are in preparation.

We have undertaken to aid the fertilizer interests by carefully analyzing one or more typical phosphate rocks and by testing at the same time the relative values of the different methods in common use, especially with respect to the influence on them of such interfering constituents as are common to materials of this class—pyrite, fluorine and organic matter.

I could easily devote an hour to the problems encountered in the selection and preparation of the samples themselves and several more to those connected with their analysis. An enormous volume of correspondence on these points has accumulated. We endeavor to keep in close touch with prominent manufacturers, and especially with prominent chemists, soliciting their advice and criticism. Almost without exception our efforts have met with hearty approval and support.

It may be well to introduce here some remarks relative to the plan we have hitherto followed in obtaining the composition of our samples. It is a plan of co-operation, in which leading works chemists and commercial chemists are invited to participate. The almost inevitable result is failure of satisfactory agreement in the reported results. Ordinarily we have given opportunity to those whose results differed markedly from the mean to revise their work without indicating to them the direction or magnitude of the deviation. This course has often resulted in much loss of time and necessitated much correspondence. For certain cases, and eventually perhaps for all, the bureau may decide to depend solely on its own chemists to establish the composition of a given material, but for some time to come this plan will be employed to a limited extent only. The bureau must first afford to its analysts sufficient time to become masters in their particular fields to an extent that will command general confidence. Until this condition is fulfilled it is far better policy to share the responsibility with experts outside of the bureau. The certificates which the bureau issues with its analyzed samples represent, therefore, the best efforts of a considerable number of analysts who are supposed to be especially expert in the analysis of the given material, and the mean undoubtedly gives in most cases a close approximation to the correct composition. The bureau does not, however, undertake to vouch for their correctness. The results by different analysts and by different methods are reported in such a way that the person using them can see at a glance what variations are to be expected in commercial work done by supposed experts and under conditions that are presumably the best that are to be encountered in commercial laboratories.

In certain cases, such as pig iron and the ordinary steels, the methods commonly used and the precautions observed are of the highest known order. The commercial results on the average are, therefore, to be accorded fully as great weight as those obtained in the bureau. It is not always so with other materials, when the character of the reagents or the apparatus play a more important part, and when the complexity of composition, as in ores, introduces special difficulties in the way of effecting complete separation of the constituents and their accurate determination. In special cases the bureau regards its own values as closer to the truth than the mean of any number of outside determinations. This is true, for instance, of the alumina and magnesia in one of the Lake Superior iron ores and even in the value for iron itself in another of them.

One without experience can form little idea of the difficulties and delays that have been encountered, from the initial selection of one of our samples through the machining, grinding, mixing, analyzing, and assembling of data to its final issuing. It took us nearly a year to get the bars to replace one of our

steels of which the supply gave out. The steel company that undertook to fill the order had to make five castings before a product of the right composition was obtained. Once delivered to the bureau, it takes from two to three weeks to reduce the sample of steel or iron to fine chips. These sometimes have to be ground finer in a special machine and in any case must be most thoroughly mixed. The successful mixing of 300 or 400 pounds of such a material requires a special mechanical mixer and no one of those on the market is entirely satisfactory. The one we have used we modified materially and are now having one made that works on a different principle entirely.

We have experimented somewhat with a view to securing homogeneous samples of relatively low melting alloys and metals in a state of sufficient division, without the use of a lathe, and have some hopes of eventual success.

Much time has to be expended by us in analyzing these materials, particularly the ores, brasses and special steels, for which the commercial methods are either more or less inadequate or have not yet received the extended study and testing that has been given to those for irons and plain steels. It is to be borne in mind that we must not be content with a single determination or with a few determinations by a single method, but that our problem is to ascertain just as closely as is possible the true composition of these complex materials. Literally months of time may thus be consumed in the study of a single sample of a new kind. The knowledge thus gained, however, shortens by far the time required for later analyses of similar or related samples. In acquiring this knowledge and in testing the various commercial methods against each other, we have already made useful observations that will be of value to others as well as to ourselves. We shall not hasten to publish our observations, but wait until we have had full opportunity to verify them repeatedly. Much information on certain of our own methods and in less degree on those used by others is to be found in our recently issued circular—'Methods of Analysis for Iron and Manganese Ores.'

In addition to the above, we have taken the preliminary steps looking toward the issuance by the bureau of a sodium oxalate for the standardization of solutions to be used not only in oximetry, but in acidimetry as well. Our reasons for making choice of sodium oxalate I need hardly go into now, save to say that for oximetry it seems to be the most satisfactory material that can be had in considerable quantity. When pure (and the different makes on the market are not to be taken at their face value, but must be tested by each buyer) the article is stable and eminently satisfactory as a standard. The use of so-called piano wire as a basis for standardizing permanganate and bichromate solutions cannot be too strongly condemned. Electrolytic iron is difficult to prepare and it too is not as pure as could be wished. The chief difficulty before us is to secure from manufacturers an article of sufficient purity in the large amounts called for. If found, it will be tested by us and issued under our seal. Should success attend our efforts in this case, we may go farther.

Having thus dwelt at some length on that feature of our work that is likely to appeal most strongly to chemists as a whole, I will pass over others more briefly.

Various bureaus of the government have called on the Standards Bureau for assistance. These requests range from simple requests for tests of materials to those that involve more or less extended research. Six months were required for a research on pyroxylin plastics with reference to their acceptance or rejection as freight on American passenger vessels. The Treasury Department wants information to enable it to draw specifications for its various record inks and to improve their quality. The Government Printing Office needs similar information in regard to its papers and inks. In fact the Standards Bureau has for



some years done the greater part of the physical and chemical testing of papers for that great printing establishment, and frequently analyzes the metals and alloys that enter into the composition of type metals or find direct use in printing. This work requires not only the time of one chemist for the routine work but of another for research connected with paper.

The following list embodies tests that were made by us in one year: Papers, writing and printing inks, mucilage, lubricating oils, fuel oil, linseed oil, turpentine and white lead, paints, gelatine compound, boiler compounds, soaps, rubber hose and valves, silks, brines, electroplating solutions and scrapings from anode plates, flooring compositions, silicate brick, glasses, gypsum, boiler tubes, steels (other than those in our list of analyzed samples), graphite, tinfoil, solder, monotype metal, antimonial lead, jute bagging, rasped pine sawdust cover for paper rolls, condenser tubes and water, guide rails. Many of these called for far more than routine testing.

In consequence of recent legislative action by Congress, it is probable that a vast deal of work in connection with the testing of structural materials will devolve upon the bureau. Its proper attention will require large additions to the chemical force and necessitate the erection in the near future of a building specially devoted to chemistry.

As is generally known, the units in terms of which practically all electrical measurements are expressed, are the International Units defined in terms of concrete standards, and not the absolute units of the C. G. S. system. The latter have been displaced, for the present at least, on account of the higher accuracy attainable with the former by the aid of carefully drawn specifications.

To secure the highest attainable accuracy, the chemist must be called upon to study the methods of purification or preparation of the materials employed, to develop special methods of analysis, qualitative as well as quantitative, and incidentally to investigate various problems such as arise in connection with every research.

The London International Electrical Conference of 1908 adopted the international ohm and ampere, defined in terms of the mercury column and the voltmeter respectively, a the two fundamental units. The Weston normal cell, which must, however, be employed to fix the results of voltmeter work, was adopted as a secondary unit.

Owing to the difficulty of reaching agreement in specifications, this question and others were assigned to an International Scientific Committee of 15 under the auspices of which a meeting of representatives of the National laboratories of Germany, England and France was recently held at the Bureau of Standards. The object was to compare the results obtained with the types of voltmeters used in the various laboratories and to compare standard cells representing the procedures adopted in those institutions as well as to investigate sources of variation in the results, in order to pave the way for the adoption of uniform specifications guaranteeing the highest accuracy of reproduction.

The results, though incomplete, are to be regarded as most satisfactory, but cannot be discussed here. The services of a chemist were needed during all the work on the voltmeter and for many months in advance of the coming of the foreign delegates. To his skill was due in large measure the unraveling of some most troublesome and obscure points in the action of different types of coulometers and of the solutions employed in them.

The main chemical questions that have a bearing on the results of voltmeter measurements are the following:

1. The preparation of pure silver nitrate.
2. Methods of testing the purity of silver nitrate
3. The influence of impurities in the electrolyte.

4. The contamination of the electrolyte by the septum employed or by the electrolysis effected.

The chemical side of the reproducibility and constancy of the Weston cell as a standard of electromotive force has been under consideration at the Bureau of Standards for some time with the result that an accuracy of reproduction of two or three parts in 100,000 is now attainable. (Parenthetically it may be said that a like degree of accuracy is striven for in the reproducibility of conditions and results by the voltmeter, that is, of at least two or three parts in 100,000 as a mean of several determinations.) The work with the Weston cell has embraced the investigation of equilibrium conditions in the cell, the methods of washing and the hydrolysis of the depolarizer, mercurous sulphate, the preparation and purification of the materials mercury, cadmium, mercurous sulphate and cadmium sulphate, and the effect of added impurities.

It is hoped that the ultimate result of the international comparison of cells and voltmeters and the exchange of the various materials will result in the adoption of uniform specifications for these materials. The bureau has made the proposal that when this shall have been effected the various national laboratories shall undertake to furnish such materials ready for use to investigators and others.

The need of a new and authoritative table of densities of alcohol-water solutions has long been apparent. Fundamental for this is an exact determination of the density of absolute alcohol. The data heretofore chiefly relied on are those of Mendeléef and the Squibbs, but these differ, hence the desirability of a new determination, which necessitates the prior preparation of pure alcohol, a most difficult problem. How this has been done is described in a paper by Mr. E. C. McKelvy, which I shall have the pleasure of presenting in abbreviated form at this meeting.

An investigation is in progress having in view the unification and simplification of methods of gas testing in this country. An important point in connection with this relates to the permissible limit for hydrogen sulphide in illuminating gas, and the accurate and quick determination of the amount present. In co-operation with the proper physical division a chemist is at work on this problem.

Another has worked in co-operation with the heat division of the bureau in the preparation of the pure materials for calorimetric comparisons, of which I have already made mention.

This latter research is closely related to another, namely, that of determining the heats of combustion of methane and ethane, ethylene and acetylene, carbon monoxide and hydrogen, which are needed as fundamental constants for a study of the calorimetry of illuminating gases. The above-named substances must be prepared in a state of great purity and for their combustion large quantities of very pure oxygen are needed. One chemist in co-operation with our very efficient glassblower has devised a generator for oxygen and hydrogen consisting of nine cells. The electrodes are of wrought iron and are separated by a glass bell-jar. The electrolyte is caustic soda of 20 per cent. strength. The cells are electrolytically in series and the current used about 20 amperes. With this current the yield of oxygen is about 47 liters per hour. The gas is passed through a platinized quartz tube two meters long, then through two towers filled with solid potassium hydroxide, then through a soda-lime tower, and finally through a calcium chloride tower. The gas is then compressed into cylinders at 100 atmospheres pressure by a special mercury piston pump. It is expected that the bureau will, in future, draw its supply of oxygen and hydrogen from this source.

A comprehensive co-operative study of underground electrolysis and corrosion is to be started this year and for this the services of two chemists will probably be needed.

Finally, a long investigation, still unfinished, is the deter-

mination of the atomic weight ratio between bromine and hydrogen. This research forms a logical extension of that already done at the bureau by Drs. W. A. Noyes and H. C. P. Weber on the ratio between chlorine and hydrogen, a work that was crowned some time ago by the award of the Nichols medal.

The force of chemists now employed numbered 13 on June 30th, which number will be increased from 4 to 6 this summer, and probably by a number of others. At present the quarters are uncomfortably crowded, but before the summer is over additional room will be provided to accommodate 17 or 18 in all.

There is a weekly journal meeting for the chemists, also certain courses of lectures and laboratory work to aid those who desire to take advanced university degrees. This latter work is done out of office hours and is accepted by some universities.

In the foregoing I have endeavored to outline in the briefest possible manner the character of the chemical work done at the bureau. You will see that it is most varied and that administration and correspondence must necessarily make such large demands on my own time as to leave little for direct experimentation. The most that I can hope to do must be at odd moments, but it is my hope and wish to be able to exercise direct supervision over the more exact analytical work, so far as this falls in line with my personal acquaintance.

The bureau will, before long I hope, do its full share in the way of publication to forward the science of chemistry both practically and theoretically. But the bureau is yet young and so are most of its chemists. Hence active publication from the start is not to be expected, for unusual care must be taken lest work of doubtful value shall emanate from an institution which should be what its name implies, a Bureau of Standards. It is too much to hope that this will never happen, but my aim will be to keep it at a minimum.

## NOTES AND CORRESPONDENCE.

### NOTE ON THE VOLATILITY OF COCAINE.

When cocaine residues were dried in a covered dish heated over the steam bath or at 100° C. in a drying oven, it was noted that a solid film soon collected on the cover. This sublimate was frost-like in appearance, insoluble in water, and on further examination was found to consist of cocaine. The fact that this body is volatile at 100° is important in connection with analytical work, if the analyst expects to heat a residue after the solvent has been evaporated, and a caution to this effect would not be out of place in the pharmacopeial directions for assaying cocaine leaves.

Two cocaine residues were tested by heating first for seven hours over a steam bath and then for seven hours in an oven at 100° C., the weights being 0.0131 gram and 0.0121 gram, the dish in the case of the first sample being open to the air and the second covered with a watch glass. At the end of the first stage of the experiment they weighed respectively 0.0108 gram and 0.0104 gram and at the end of the second stage 0.0083 gram and 0.0089 gram. There seemed to be practically no difference in the proportional loss whether the dish were covered or not.

A cocaine residue heated several hours in a drying oven at temperatures of 60°, 80° and 90° suffered no loss in weight, and when heated to 98° there was only a slight loss though there was considerable sublimation upward on the walls of the dish.

It was evident from the observations that the last portions of the solvent should be evaporated as rapidly as possible from a cocaine residue, using a blast; and that the residual material should be dried cautiously, not over 90° and for safety should be brought to a constant weight by drying over sulphuric acid.

H. C. FULLER.

### NOTE ON DR. BACKE'S INVESTIGATION OF MALTOL AND ISOMALTOL.

*Editor Journal of Industrial and Engineering Chemistry:*

Since the publication of my short paper on "A Source of Error in the Examination of Foods for Salicylic Acid," which was sent you September, 1909, and appeared in this *Journal* for January, 1910, it has come to my notice that a communication relating to the same source of error was published by Dr. Arnold Backe in *Annales des falsifications* for November, 1909, and Dr. Backe has recently informed me by letter that the experiments upon which his communication was based were made in July of last year. Since my own experiments were made the month following, I beg space to acknowledge the priority of Dr. Backe's work on this point over my own, and also to call attention to his more recent papers,<sup>1</sup> in which he discusses the isolation and properties of the substances to which the interfering reaction is due.

H. C. SHERMAN.

### ACCURACY IN SAMPLING.

*Editor Journal of Industrial and Engineering Chemistry:*

On the appearance of Mr. Bailey's paper on "Accuracy in Sampling Coal"<sup>2</sup> I gave it considerable study. By the time I had arrived at my conclusions in regard to it, interest, judging by cessation of correspondence, had waned. I therefore hesitated to publish my views. The recrudescence of Mr. Bailey's paper in that of Mr. F. B. Porter,<sup>3</sup> however, seems to warrant calling attention to some errors in the former. Mr. Bailey began his paper by comparing some results obtained in the A. D. Little Laboratory with the results tabulated on pp. 281-284, Professional Paper No. 48, U. S. Geological Survey. This tabulation led Mr. Bailey into an error which may best be explained by a concrete instance. 4833 lbs. of an Iowa coal were sampled and analyzed. This lot showed 20.70 per cent. ash, 10986 lbs. from the same carload showed 16.04 per cent. ash, 12000 lbs. showed an ash of 14.46 per cent. Of course, the proper way to obtain an average analysis is to multiply each analysis by the weight of the coal which it represents, add the products and divide by the total weight of coal. Calculated in this manner the coal in question showed 16.17 per cent. ash. The carload from which these portions were taken was sampled as a whole and showed 15.22 per cent. ash. The best value available for this coal is an average of the two figures, 15.69 per cent., and the error due to sampling is 0.47 per cent. In the averaging of the Geological Survey the figures were averaged, as much weight being allowed to the analysis representing 4833 lbs. as to the analysis representing the carload. Calculated in this way the average was 16.60 per cent., and the difference between that figure and 20.70 per cent., or 4.10 per cent., Mr. Bailey considered error.

Recalculating this tabulation the maximum error is 1.16 per cent. and only 5 analyses out of 34 show an error greater than 0.7 per cent. It is probable that these higher errors would disappear if we could trace all the coal involved, but as it stands the maximum error is much less than that of the commercial laboratory as might reasonably be expected from the favorable conditions under which the government chemists worked. Whereas Mr. Bailey thought the government error was more than twice as large as the other.

Mr. Bailey closes his comparison of these two sets of figures with the following statement:

"As this data follows the probability curve very closely, the formula for probable and possible error can be safely applied in determining the reliability of different methods of sampling."

Even if Mr. Bailey had substantiated his formulae by correct figures there would be good reason to be suspicious of them on a

<sup>1</sup> *Compt. rend.*, 150, 540 and 151, 78.

<sup>2</sup> *This Journal*, 1, 161 (1909).

<sup>3</sup> *Ibid.*, 2, 148 (1910).

*priori* grounds, for, as Nernst and Schoenflies put it, "we can with certainty regard  $\Delta x$  (the error) as a small amount, otherwise the whole measurement would be illusory" or as another writer puts it "there are no large errors;" that is, the method of least squares is not applicable where errors are large. The errors in Mr. Bailey's large table of analyses run up to almost 40 per cent. of the total ash. These are large errors and consequently the so-called probable error does not comply with the definition, which is "in any series of errors the probable error has such a value that the number of errors greater than it is the same as the number less than it. Or, it is an even wager that an error taken at random will be greater or less than the probable error." Of 193 analyses 111 are greater than Mr. Bailey's calculated probable error and 82 less. The formula for possible error is, except for the constant, the same as that for probable error and must likewise be rejected.

At the time of the appearance of the paper I suggested to Mr. Bailey, in private correspondence, that 1300 experiments were insufficient to demonstrate the theory of probabilities. Mr. Bailey replied that the smoothness of the curve obtained, was good evidence that the experiments were sufficient. In the paper Mr. Bailey describes the curve as being like a parabola, but the points determined do not fit into the equation for the parabola and calculation shows that the curve is, in fact, a broken line. Furthermore, the figures obtained prove themselves inadequate. Varying numbers of pieces of whitened coal were sent over the rifle sampler. The pieces found on the right side of the machine were counted. Each set was sent a few hundred times. When four pieces were used the maximum number found was four; the minimum none. When eight were used the maximum number was eight, the minimum one; when sixteen were used the maximum was twelve the minimum three. Judging from the experiments with eight pieces it might be supposed that the machine was untrue and threw to the right but the next experiment showed that this was not the case. The experiments were obviously inadequate.

A few simple experiments will give an idea of the difficulty of proving the theory of probabilities.

A coin was tossed 50 times and came up heads 26 times, tails 24 times, and at no time were the heads and tails equal.

A die was thrown 96 times, the faces came up as follows:

Face.....	1	2	3	4	5	6
Times.....	13	18	12	9	26	18

I have at my disposal a record of 9000 poker hands actually dealt.

Theory demands that 50.12 per cent. of the hands should have been worthless, whereas 51.42 per cent. was the figure actually obtained.

A consideration of these figures and of the greater complexity of the rifle sampler problems make it evident how 1300 experiments must be.

In conclusion I wish to protest most vigorously against the phrase "size-weight per cent."

The only excuse for the coinage of a new word or term is the birth of a new idea.

There is absolutely no idea intended to be conveyed by this phrase which is not entirely covered by the one word size. Size must, of course, be expressed in regard to something else and Mr. Bailey had a perfect right to express the size of his largest pieces in percentages of his sample before dividing, and with this word of explanation the cumbersome phrase might have been avoided together with the numerous explanations which it required.

Mr. Porter says that there is a prevalent idea that the larger the sample and the smaller the pieces the better. This is more than a prevalent idea, it is a fact. Both gentlemen have done well to emphasize this fact; but that they have shown any

relationship which can be expressed in a mathematical equation, can not be maintained.

LOWELL, MASS

FRED. C. WELD.

## EXPLOSIBILITY OF COAL DUST.

The recently created Federal Bureau of Mines has just issued a bulletin on the explosibility of coal dust, with chapters by J. C. W. Frazer, Axel Larsen, Frank Haas and Carl Scholz. The bulletin was prepared by the Technologic Branch of the United States Geological Survey, which is now a part of the Bureau of Mines, and therefore will be known as Geological Survey Bulletin 425, but will be distributed by the Bureau of Mines. The author of the bulletin, George S. Rice, chief mining engineer of the Bureau, goes fully into one of the most serious and most perplexing problems that the coal mines have had to contend with in the last few years. He traces the growth in the belief in the explosibility of coal dust, summarizes the experiments and mine investigations that have established this belief and gives the present status of preventive measures.

In the introduction, Mr. Rice says: "Only within comparatively few years has the dry dust of bituminous and lignitic coal been generally recognized as an explosive agent more insidious, threatening and deadly to the miner than firedamp. Firedamp carries its own flag of warning—the 'cap' in the safety lamp—but coal dust, though visible, does not attract attention until present in large quantities. Firedamp is of local occurrence and except in notable and very exceptional cases is controllable by careful manipulation of the ventilating currents. If by mischance a body of firedamp is ignited in a mine, the force of the explosion is terrific, but the effect is localized unless dry coal dust is present, or unless (as it very rarely happens) an explosible mixture of methane gas and air extends through large areas of the mine. In a dry mine dust accumulates everywhere, and the blast from the ignition and combustion of bituminous dust may traverse miles of rooms and entries and wreck structures at the entrance of the mine. The comparative potential destructiveness of gas and of bituminous dust is strikingly shown by the history of the Pennsylvania anthracite mines. These mines not infrequently have large inflows of gas, and the resulting mixtures of gas and air have sometimes been ignited, yet no such wide sweeping explosions have taken place, despite the presence of dry anthracite dust, as have happened in excellently ventilated bituminous mines."

Mr. Rice reviews the experiments into the explosibility of coal dust in foreign countries and dwells at considerable length upon the attitude taken in France by the engineers, who, until the great disaster at Courrières in 1906, which cost 1,000 lives, did not believe that coal dust would explode without the presence of firedamp. Since that terrible disaster a testing station has been established in France and now the French engineers are fully convinced of the dangers of coal dust.

"The coal dust question in this country," continues Mr. Rice, "can not be said to have awakened wide-spread interest among mining men until the terrible disasters of December, 1907, which resulted in the death of 648 men. In response to a demand by those interested in coal mining throughout the country, Congress, in 1908, made an appropriation for the investigation of mine explosions. The United States Geological Survey was charged with the investigation. A testing station was at once decided upon and was established at Pittsburgh, Pa.

"While it is probable that for several years the leading mining men in the country have believed in the explosibility of coal dust without the presence of firedamp, yet until the public demonstrations were given at the testing station at Pittsburgh, during 1908-'09, and reports were received of similar tests made abroad, a large proportion disbelieved. These tests were so convincing to those who saw them, and such general pub-



licity has been given to them, that it is now exceptional to find a mining man who does not accept the evidence of the explosibility of coal dust. The question of the day no longer is 'Will coal dust explode?' but 'What is the best method of preventing coal dust explosions?' "

The following are some of the tentative conclusions of Mr. Rice on the dust problem:

"That coal dust will explode under some circumstances, both in the presence of firedamp and without it, is now generally accepted by mining men. The writer fully agrees with this and takes the following views of the explosibility of dust and the conditions necessary for explosion.

"Experiments at Pittsburg indicate that under ordinary conditions the dust must be from coal having at least about 10 per cent. of volatile combustible matter, though in certain foreign experiments, it is claimed explosions were obtained with charcoal dust.

"Dusts with higher percentages of volatile combustible matter are more sensitive, ash, moisture contents, and size being constant. This view is based partly on the preliminary experiments at Pittsburg and on the results of experiments of M. Taffanel and other foreign investigators. Where there is a large amount of dry coal dust, judging from the Pittsburg experiments, a humid atmosphere has little effect on ignition of dust or propagation of an explosion. A long continuance of the humid conditions renders the coal dust moist and inert, but the presence of moisture in the air at the moment of explosion is not sufficient to prevent an explosion; that is, not enough moisture is carried by the mine air to reduce materially the temperature of the flame. Fully saturated vapor at 65° F., an ordinary mine temperature in this country, weighs 6.78 grains per cubic foot (15.5 grams per cubic meter). Coal dust suspended in such a saturated atmosphere in a cloud of moderate density weighs, say, 200 grams per cubic meter. At the figures given the weight of vapor is but 7.8 per cent. of the weight of dust. The Pittsburg experiments with wetted dust showed that several times this percentage of moisture in the dust, in addition to a nearly saturated atmosphere, was required to prevent propagation.

"Probably with a low dust density, the relative humidity of the air would be an important factor in tending to prevent the initiation of an explosion. However, the great purpose of artificially humidifying mine air is that it may serve as a vehicle for carrying water to the dust."

Mr. Rice concludes by reviewing the various remedies that are offered for the coal dust problem, giving the good and bad points of each.

This bulletin may be obtained by addressing the director of the Bureau of Mines, Washington, D. C.

## BOOK REVIEWS AND NOTICES.

**Chemische Technologie der Neuzeit.** Lieferung, 1, 2, 3. Edited by Dr. Otto Dammer with the cooperation of 49 experts. Stuttgart: Ferdinand Enke, 1910.

The volumes on chemical technology which are being published under the editorship of Dr. Dammer, to complete and bring down to date his large five-volume work issued 1895-1898, are excellent. Three volumes will complete the work which has the title "Chemische Technologie der Neuzeit." A few sins of omission may be charged against the chapters which have thus far appeared, but these are easily excused in consideration of the difficulties in the way of securing authentic, accurate detailed information concerning modern chemical industries and processes. This work represents by far the best attempt which has yet been made to give the student and reader accurate information in regard to the recent developments in the field of

applied chemistry. In connection with the five volumes of Dammer's "Handbuch der Chemischen Technologie" they constitute an invaluable aid to the student of industrial chemistry. The subjects thus far treated are: water, liquid air, ozone, hydrogen, sulfur, selenium, carbon bisulfide, carbon tetrachloride, sulfur chloride, thiosulfates, hydrosulfites, sulfurous acid, sulfites, sulfuric acid, Stassfurt salts, salt, soda, sodium sulfate, hydrochloric acid, chlorine, calcium chloride, potash, saltpeter, nitric acid, air nitrates, ammonia, iodine, fluorine, carbon dioxide, cyanides, borates, phosphorus, the alkali earth salts, aluminum salts, artificial precious stones, rare earths and glow-lights, electric glow-lights, peroxides, carbides, silicides and explosives.

**Van Nostrand's Chemical Annual.** By JOHN C. OLSEN. Second issue, 1909. Cloth, 12mo. pp. vi + 580. New York: D. Van Nostrand Co., 1909. Price, \$2.50 net.

In the second issue of this well-known book of tables the pages have been increased from 496 to 580—those devoted to chemical and other tables from 415 to 465; the rest of the increase is in the pages devoted to the review of chemical literature. The frontispiece of the book is a portrait of Mendeléeff and on a flyleaf there is given a sketch of his life. The tables have been used by a large number of chemists since the first issue was published and have been found accurate. The table for sulfuric acid by Ferguson and Talbot adopted by the Manufacturing Chemists' Association of the United States is included. If any suggestion were to be made it would be for a more compact form with thinner paper and flexible cover for the next issue of the annual.

**Fuel and Refractory Materials.** By A. HUMBOLDT SEXTON. New and Revised Edition. 12mo. pp. x + 364. New York: D. Van Nostrand Co., 1910. Price, \$2.50 net.

The changes in the present edition are chiefly in the chapters on gas producers, pyrometry and coke ovens. In describing modern plant and apparatus it has been found necessary in order to save space and also because of lack of interest in the older forms to omit many of these. The chapters are: 1, Combustion; 2, Heating Power of Fuels; 3, Fuels, Wood, Peat, Coal; 4, Solid Prepared Fuels; 5, Coal Washing; 6, Liquid Fuels; 7, Gaseous Fuels; 8, Recovery of By-Products; 9, Furnaces for Metallurgical Purposes; 10, Furnace Operation; 11, Pyrometry; 12, Calorimetry; 13, Utilization of Fuel; 14, Testing Fuels; 15, Refractory Materials, Bricks, Crucibles. As the table of contents indicates, practically all of the book is devoted to fuels and furnaces and a small part only to refractories. There are 104 well selected illustrations representative for the most part of English design and practice. Under calorimetry Parr's calorimeter is omitted. In general an excellent textbook brought nearly down to date.

The Bureau of Standards has issued two circulars of the greatest interest to chemists. Circular No. 25 is entitled "Standard Analyzed Samples—General Information." This bulletin is published for the general information of those interested in standard analyzed samples; it is divided into the following parts: Introduction, Function of Standard Analyzed Samples, History of Bureau of Standards' Samples, The Choice of Standard Materials, Preparation of Materials, Uses of Standard Samples, General Considerations, Standard Analyzed Samples issued or in preparation, Summary of Analyses, Ordering and Shipping. Under the head of "Uses of Standard Samples" the circular states: "The principal uses of the bureau's analyzed samples appear to be as follows: First: In the settling and avoiding of disputes between buyers and sellers. Such disputes very frequently arise through the selection of inappropriate or faulty methods of analysis by one of the chemists, and the analysis of a standard material usually brings these to light

before the case comes to court. Second: In standardizing volumetric solutions; for example, the determination of sulphur and manganese in iron and steel; iron ores are used for establishing the iron standard for permanganate or bichromate solutions, from which the standards for most other titrations are calculated. Third: As material for trying out new methods. The use in this connection is obvious. Fourth: As practice material for new and inexperienced chemists. They have quite an extended use in universities in this connection." A list of thirty-seven samples already issued or in preparation is given together with prices.

Circular No. 26 is entitled "Analyzed Iron and Manganese Ores—Methods of Analysis." The following are the contents of this circular: I, Introduction; Mixing, Drying, Reagents, Apparatus. II, Methods of Analysis at the Bureau of Standards; Silica, Phosphorus, Aluminum, Titanium, Standardization of Permanganate Solutions, Iron, Available Oxygen, Manganese, Lime, Magnesia. III, Methods used by other analysts; Commercial chemists, Works chemists, Mine chemists.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### DIVISION OF PHARMACEUTICAL CHEMISTS, AMERICAN CHEMICAL SOCIETY.

San Francisco Meeting, July 16, 1910.

In the absence of the Chairman the Secretary requested Dr. H. E. Barnard, of Indianapolis, to preside over the meeting. The customary reading of the minutes was followed by the report of the treasurer and Committee on Quantitative Methods.

The following papers were read and discussed:

Albert Schneider, "The Relationship of the Microscopical and Chemical Analyses of Vegetable Drugs, Foods and Spices."

W. A. Pearson, "Asaetida."

B. L. Murray, "Electrolytic Determination of Mercury in the Mercury Salts of the Pharmacopoeia."

E. K. Nelson, "Capsaicin, the Pungent Principle of Capsicum."

E. K. Nelson, "The Detection of Capsicum."

H. C. Fuller, "Note on the Volatility of Cocain."

H. C. Fuller, "Separation and Determination of Cocain and Strychnin and of Atropin and Strychnin when they Occur Together."

Dr. F. Klein, "New Tests."

G. H. P. Lichthardt, "Identification of Caramel."

L. A. Brown, "Determination of Acidity in Hydrogen Peroxide."

Following the ideas brought out by Prof. Schneider in his paper a motion was passed as follows: Moved that the chairman and executive committee, after consulting with the Division of Agricultural and Food Chemistry, consider the question of appointing a committee on micro-analysis, with power to appoint such a committee if advisable. The idea of this was to attract micro-analyst to the ranks of this division.

B. L. MURRAY.

### DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY.

San Francisco Meeting, July 15 and 16, 1910.

The session on Friday morning, July 15th, was devoted to an inspection of the Laboratories at the University of California, Berkeley, Cal. In the absence of the Secretary the reading of the minutes was omitted and E. F. Ladd was appointed to act as Secretary, *pro tem*.

The meeting on Saturday was held in the Green Room of St. Francis Hotel, San Francisco, and was called together by G. E. Colby. The following papers were read:

C. A. Browne, "The Saccharimeter Scale and the Means for its Verification."

C. A. Browne, "The Normal Weight of Dextrose."

H. H. Bunzell, "The Role of Hydrogen Peroxide in the Oxidation of Pyrogallol by the System  $H_2O_2$ -Peroxidase."

H. E. Barnard, "The Influence of the Ingestion of Spices upon the Excretion of Hippuric Acid."

H. W. Wiley and J. A. LeClerc, "Environmental Work on Wheat."

J. A. LeClerc and J. F. Breazeale, "Translocation of Plant Foods and the Elaboration of Plant Material during the Germination of Wheat."

P. L. Hibbard, "Time Factors in Determination of Nitrogen, and Other Observations on the Kjeldahl Method."

G. W. Shaw, "Effect of Environment on the Composition of Wheat."

J. A. LeClerc and B. R. Jacobs, "High Protein Bread."

Dr. E. W. Hilgard, "Unification of Chemical Soil Analysis."

The following papers were read by title only:

G. O. Higley, "The Relation of Carbon Dioxide Excretion to Body Weight."

G. O. Higley, "The Carbon Dioxide Excretion as Modified by Barometric Changes."

R. E. Swain, "The Physiological Action of Thallium Salts as Shown by the Nitrogenous Metabolism."

R. E. Swain, "The Utilization of Starch Introduced Directly into the Circulation."

E. M. Chace and A. R. Albright, "The Detection of Lemon Oil in Orange Oil."

C. E. Bradley, "The Reactions of Lime and Gypsum on Some Oregon Soils."

R. S. Hiltner, "Citral in Lemon Oils and Extracts."

J. B. Rather and G. S. Fraps, "The Composition and Digestibility of the Ether Extract of Cowpea Hay."

F. C. Cook, "The Destruction of Invertase Solutions in the Absence of a Preservative."

F. C. Cook, "The Destruction of Invertase Solutions by Shaking and by the Electric Current."

Edward Bartow and B. H. Harrison, "Determination of Ammonia Nitrogen in Water in the Presence of Hydrogen Sulphide."

Edward Bartow and C. E. Millar, "Extent and Composition of the Incrustation on Filter Sands."

Chas. B. Bennett, "A Note on the Hypoxanthine of Meat."

Alfred N. Cook, "The Relative Toxicity of Substances Found in Foods."

M. E. Jaffa, "Résumé of the Work of the California State Food and Drug Laboratory."

Louis H. Jackson, "Testing for Saccharin."

Waldemar Koch, "Quantitative Chemical Analysis of Animal Tissue: V. Estimation of Chlorine."

M. M. MacLean, "A Convenient Drying Oven."

J. B. Rather and G. S. Fraps, "The Constituents of the Wax of Candelilla, or Mexican Wax Plant."

P. A. Yoder, "A Polariscopic Method for the Estimation of Malic Acid and Its Application in Cane and Maple Products."

P. A. Yoder, "Notes on the Acid Constituents of Sugar Cane Juice and on Methods for Their Determination."

C. L. Alsborg and O. F. Black, "Biochemical and Toxicological Studies upon a Number of Species of *Penicillium*."

Charles L. Parsons, Secretary of the American Chemical Society, spoke on The Methods of Securing Funds for Promoting the Work of the Division. A motion was made by H. H. Bunzell to make an annual assessment of fifty cents on all members of the Division of Agricultural and Food Chemistry for the purpose of defraying the expenses of this division.

There were present at the meeting Saturday morning about forty members.

E. F. LADD.

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

REPORT OF COMMITTEE ON CHEMICAL ENGINEERING EDUCATION.<sup>1</sup>F. W. FRERICHS, *Chairman.*

WM. M. BOOTH.

F. G. WIECHMANN.

GEO. D. ROSENGARTEN

A. A. I. VEILLON

Circular letter No. 1 to the members of the Committee on Chemical Engineering Education of the A. I. C. E.

3828 WESTMINSTER PLACE, ST. LOUIS, MO.,

FEBRUARY 4, 1910.

DEAR SIR: The Committee on Chemical Engineering Education was created at the Pittsburg meeting December, 1908. It was the result of a general feeling which prevailed among the members of the A. I. C. E., that the course of education generally pursued by prospective chemists at the present time does not produce men who are prepared in the best possible way for practical work in the manufacturing establishments of the United States.

As chemistry is a science which is most highly developed in Europe, and especially in Germany, it is natural that the methods of education of chemists in the United States, especially in post-graduate work, have been to a large extent copied from the methods adopted in that Continent. This is more the case, since a large percentage of the older teachers of chemistry have been educated abroad. The highly developed chemical industries such as the coal-tar industries, the manufacture of artificial perfumes and pharmaceutical preparations, require chemists of the highest theoretical education in organic chemistry, who, at the same time are satisfied to do actual work for long hours and for small salaries.

This condition can obtain in Europe, since there is an abundance of chemists trained for that kind of work and anxious to make a living. This very fact enables European manufacturers to export these goods to the United States, as long as the American chemist is not sufficiently protected by tariff laws. On the other hand, many European firms support large research laboratories for the systematic development of new processes and new articles. They can do so, since the cost of experimenting and the salaries of chemists who can do research work, are comparatively low. If patents have been obtained in the United States, the goods are made abroad and imported, and the American chemist is barred from the manufacture of this class of articles.

As long as our tariff and our patent laws are not improved, there would not seem to be any hope that such goods can be made successful in the United States.

These conditions have caused the enormous growth of organic chemical manufacturers in Europe, and since a very large percentage of all the chemists find employment in this class of works, the courses at European universities seem to be shaped to suit their special requirements. For the student such a course appears to be highly acceptable, since it greatly favors organic chemistry, which branch permits of brilliant speculation, and is, therefore, most fascinating to the beginner. Besides, it coincides largely with the course which is most approved for the education of teachers of chemistry, and therefore prepares for professorships and for a large branch of a specific chemical industry at the same time.

For the universities it may be no small consideration that the students working on their theses for the degree are welcome assistants for the scientific work carried on in their laboratories.

As an excuse for this, the remark is frequently heard that every student owes it to science to devote one or two years to theoretical work, even if he does not reap direct benefit from it.

It seems natural that the scientific work, to which the individual laboratories devote their efforts, more frequently is guided by the personal liking of the professor in charge than

by the earnest desire to fit the student most effectively for his chosen profession. Now the personal liking of the professors in charge would go, most probably, in the direction of organic chemistry, in which they can most easily become conspicuous, and therefore it would seem that at European universities the interests of all chemical industries not needing a specific knowledge of organic chemistry, are sacrificed to the interests of the specific organic manufacturers, which have become of so vital importance to the economic system of European countries.

But from those branches of manufacture the American chemist is largely barred, and for this reason his course of education ought to be different from that of European chemists in order to suit the requirements of his own country.

It is evident that the American student is in the same position as the European chemist entering the great variety of chemical industries other than coal-tar products, artificial perfumes, and pharmaceutical preparations. It might be well to recognize that many experienced manufacturers abroad do not consider the courses offered at European universities to be the most desirable for this class of chemists. This feeling apparently has been recognized by the authorities and has found its expression in the inauguration of the degree of Engineer Chemist at polytechnic schools in Germany.

Under these conditions, it would be of great benefit if the peculiar requirements could be pointed out, which would best fit the prospective chemist to enter practical life in the United States. An expression of opinion coming from the A. I. C. E., which embraces a large body of practical men, would seem to have a special value, and in order to crystallize this opinion into a definite form, the Committee on Chemical Engineering Education has been appointed.

It is thought that the best course for the work of this committee would be:

- 1st. To formulate the opinion of this committee in regard to the most suitable course of education for a "chemical engineer."
- 2nd. To submit the opinion of the committee to the entire membership for discussion by letter.
- 3rd. To submit the result of this discussion to a general meeting of the A. I. C. E. for final discussion and action.

If in this way the opinion of the A. I. C. E. has been formulated, it may be submitted to the institutions of learning in the United States, and the educators in these institutions might be induced to lay out courses which are likely to produce the desired results with the least outlay of time and money on the part of the prospective chemical engineers.

In order to establish the opinion of the committee on the most effective course of education, it seems necessary first to define the meaning of the term "chemical engineer."

The constitution of the A. I. C. E. in Article III, Section 1, defines the qualifications for active membership and from these the intended meaning of the term "chemical engineer" may be inferred.

In Art. III, Sec. 1, Paragraph 1, our constitution provides for such candidates who have not had the opportunity of an early education, but who, as self-made men, have acquired by persistent work such ability in handling chemical problems as rightly entitles them to recognition as chemical engineers. The A. I. C. E. in this paragraph pledges itself to recognize the work of a true genius, independently from the way in which it has been accomplished.

The same seems to apply to candidates accepted under Paragraph 2, who have had only the opportunity to acquire the degree of B.A.

Art. III, Sec. 1, Paragraph 3, apparently indicates the course of education which is thought to produce the average "chemical engineer." But even here the definition is somewhat vague and evidently induced by the feeling that a satisfactory understanding of the term "chemical engineer" has not been established.

<sup>1</sup> From August 1910 *Bull. Am Inst Chem Eng*



A civil engineer who has specialized in water and sewage purification may be a very desirable member of the Institute, and so may be the mechanical engineer who has specialized in power plant economics, and the architect who made sanitary installations a specialty. But with these branches of engineering the study of chemistry is only of secondary consideration, and for this reason a course of education would preferably be devised in every specific instance.

Somewhat different is the study of electrical engineering, since electricity is so closely allied with chemical manufacture that electrochemistry has become a study by itself.

It would seem to be the education of the prospective chemist who is to hold the degree of B.S. in chemistry which comes under discussion by this committee, since it prepares the student for the science of chemical engineering in its more specific sense. In order to simplify the discussion I propose to confine, at the present, the work of the committee to the education of chemical engineers in this sense, leaving it to the pleasure of the committee to discuss the other branches at a later time.

In order to have a basis for discussion, I introduce the courses of a typical American university, and shall ask a number of definite questions in order to learn the position of the members of this committee in relation to the course of "chemical engineering" offered by this university.

#### SYNOPSIS OF THE COURSE IN CHEMICAL ENGINEERING.

##### FRESHMAN YEAR.

###### First Term.

Subject	Hours per Week.	
	Rec.	Lab., etc.
English Composition.....	3	
German Grammar, or } French.....	3	
Trigonometry.....	5 (9 weeks)	
Algebra.....	5 (9 weeks)	
Chemistry (General Descriptive).....	2	3
Physics.....	1	3
Drawing, Freehand.....		4
Lettering.....		2
Total, 14	12	

###### Second Term.

English.....	3	
German, or } French.....	3	
Analytical Geometry.....	5	
Physics.....	1	3
Chemistry (General Descriptive).....	2	3
Drawing.....		6
Total, 14	12	

##### SOPHOMORE YEAR.

###### First Term.

German Grammar, or } Reading in Modern French.....	3	
Differential Calculus.....	4	
Descriptive Geometry.....	3	
Sound, Heat, Optics.....	4	
Qualitative Analysis.....		6
Machine Drawing.....		3
Total, 14	12	

###### Second Term.

Quantitative Analysis (Gravimetric and Volumetric).....	1	5
Surveying.....	2	5
Integral Calculus.....	3	
Statics.....	3	
Optics.....	3	3
Assaying and Stoichiometry.....	1	3
Total, 13	16	

##### JUNIOR YEAR.

###### First Term.

Subject	Hours per week.	
	Rec.	Lab., etc.
Organic Chemistry.....	3	
Laboratory Organic Chemistry.....		6
Assaying and Stoichiometry.....	1	3
Quantitative Analysis (Commercial and Industrial Products).....		6
Mineralogy.....	2	3
Electrical Machinery.....	3	
Mechanics.....	3	
Total, 12	18	

###### Second Term.

Organic Chemistry.....	3	
Laboratory Organic Chemistry.....		6
Advanced Quantitative Analysis (Commercial and Industrial Products).....		6
Electrical Machinery.....	3	
Mineralogy.....	2	3
Dynamics.....	3	
Electrical Laboratory.....		3
Total, 11	18	

##### SENIOR YEAR.

###### First Term.

Advanced Quantitative Analysis (Food, Water, and Gas).....		6
Physical Chemistry.....	1	3
Industrial Engineering.....	2	
Economic Geology.....	2	3
Engineering Materials.....	3	
Economics.....	2	
Bacteriology.....		6
English.....	1	
Total, 11	18	

###### Second Term.

Advanced Quantitative Analysis (Food, Water, and Gas).....		6
Seminar.....	1	
Industrial and Engineering Chemistry.....	2	
Research.....		4
Physical Chemistry.....	1	3
Geodesy.....	1	
Economic Geology.....	2	3
Hydraulics.....	3	
Economics.....	2	
English.....	1	
Total, 13	16	

In the School of Engineering of this university a regular high school education is required from entering students.

The degree of B.S. is conferred on the satisfactory completion of the four years' work.

The degree of Ph.D. is open, after not less than three years of residence and study, to all who have received the degree of B.S.

By glancing over the full engineering courses it will be found that they are arranged on very broad lines, so that specialization would not seem necessary before the Junior year. At this time the student of chemistry would specialize, obtaining at the end of his four years' course the degree of B.S. in chemistry, being at this time equally well prepared for post-graduate work in pure chemistry and in chemical engineering.

If the graduate from the B.S. course desires to complete his studies in pure chemistry, or if he desires to prepare himself better for practical work, he may take a post-graduate course of three years' study and obtain the degree of Ph.D.

Having explained existing conditions as I see them, I now take the liberty of asking the following questions:

1st. Is, in your opinion, a chemist having completed a four-year course as offered at this university and possessing the degree of B.S. satisfactorily equipped to enter practical work?

2nd. If question 1 is answered in the negative, can, in your

opinion, a four-year course be arranged in such a way that a chemist after its completion is satisfactorily equipped to take up practical work?

3rd. If questions 1 and 2 are answered in the negative, can, in your opinion, a four-year course supplemented by one year post-graduate work taken at the same university equip a chemist to be efficient for practical work?

4th. Are the post-graduate courses as offered at American universities, in your opinion, the most effective courses which can be designed for the education of chemical engineers?

5th. If question 4 is answered in the negative, what changes are, in your opinion, necessary to make the offered courses effective?

6th. Are the courses offered at European universities and polytechnic schools, in your opinion, the most effective courses for producing chemical engineers, fit for work in American places of manufacture?

7th. Have you any specific suggestions for improving the courses, which are offered at present by American universities?

Respectfully submitted,

F. W. FRERICHS,  
Chairman.

APRIL 15, 1910.

DR. F. W. FRERICHS, *Chairman*, Committee on Chemical Engineering Education of the A. I. C. E., St. Louis, Mo.

MY DEAR DOCTOR FRERICHS:

I will give briefly my views upon the subject of chemical engineering education in answer to your circular letter of February 4th.

The differences observable in the development and practice of chemistry in Europe and the United States are very well set forth in that letter, and I agree with all your suggestions upon that subject. I would add one further point of difference which, of course, springs from the same cause, and that is the larger scale of operations which we find always manifested in this country by great tonnage production. This will continue to grow as a marked feature of our work. When one understands that the genius of America is most often applied to increase of production rather than to refinement of products, it would seem to me to be a corollary from this that our students should be well trained in mechanics to meet the demand which the world seems to put upon us to supply staples. The type that we should in the future choose to imitate would be rather that of the metallurgical engineer.

In answer to your questions, I would make the following statements:

1. No.
2. Only in case the preliminary examination for entrance on the B.S. course is more severe than the present high-school graduation test.
3. Such a course as last named, with one year post-graduate course, would be adequate to properly equip a chemist.
4. Not at all.
5. More devotion to problems truly combining theory and practice.
6. No.
7. I may state my views in general as follows:

For a course in chemical engineering, the best efforts should be spent in the beginning, either in the high school or in the first year of the B.S. course. Advanced work should have been done in literature, philosophy, the nature of matter and substances, logic and mathematics and advanced algebra. The beginning of real scientific work should include most of what we have to-day in such schools as the university whose course you have quoted and might be in four years as follows:

1st year. Physics, drawing, chemistry, metallurgy, geometry.  
2nd year. Analysis, applied electricity, surveying, calculus.

3rd year. Advanced metallurgy, mechanics, organic chemistry.

4th year. Construction, theory, and design. Materials, accounting, organic chemistry, physical chemistry, electrical chemistry.

For a doctor's degree, two years' research in metallurgy, process work, design, practical execution or economic studies.

In general, I should say, that if we could try to grasp the genius of European regard for deep study and combine it with the American genius for adaptation to any conditions, no matter how embarrassing, we would have produced a result combining the greatest strength and promise for the future.

Yours sincerely,

CHAS. F. MCKENNA.

MARCH 3, 1910.

DR. F. W. FRERICHS, *Mfg. Chemist*,  
3828 Westminster Place,  
St. Louis, Mo.

DEAR SIR:—Your favor of February 5, 1910, duly received. In accordance with your request, I herewith submit my answers to your questions, and my suggestions in the matter.

In reply to your questions:

1. No.
2. No.
3. Yes.
4. I am not sufficiently acquainted with the different post-graduate courses now offered at the American universities to form an opinion.
5. My answer to this question is implied by my answer to No. 4.
6. As far as my limited knowledge as to the courses offered at the European universities and polytechnic schools permits me to frame a reply to this question, I would state that in my opinion, the Polytechnic High School at Charlottenburg (Berlin, Germany) offers the best at the present time. The degree granted upon completion of this course is Docktor-Ingenieur.
7. My reply to this is as follows:

I would suggest that there be demanded for entrance to the university a thorough knowledge of German grammar and French grammar, and that the ability to read easy works in both languages, at sight, be required. This would permit the reading at sight in the first year of technical scientific text-books in German and in French.

I would further advise that German be thus taught in the first term of the first year and French in the second term of the first year, or *vice versa*, as might prove most convenient to the departments in charge.

In the second year I would also assign one term to the study of German and one term to the study of French, continuing and progressing along the lines followed in the first year, and in addition thereto, conferences on technical subjects in chemistry and physics, in these two languages.

I would also suggest adding to the first term's work, in the second year, the study of qualitative analysis and stoichiometry. In the second term of the second year I would consider it to be an advantage to omit the study of statics and to replace the same by instruction in chemical philosophy, and furthermore to complete the study of assaying in the second year.

In the third year, first term, I would replace the study of assaying, which would now have been achieved, by the study of statics and mechanics, *i. e.*, mechanics too, if this could be arranged. If not, I would have mechanics taught in the second term of the third year.

In the fourth year, first term, I would substitute for the study of bacteriology, the course of botany 5 for botany 7, and botany 7 in the second term. In the second term of the fourth year, I would omit the study of geodesy, which I do not consider necessary for students in chemical engineering.

I have not been able to give sufficient thought to enable me to outline completely the courses of study which should be included in the post-graduate year for chemical engineers, but proceeding upon the belief that chemical engineering is essentially the adaptation of laboratory processes to factory conditions, I believe that these courses should include the study of theoretical and practical electrochemistry, the designing and laying out of factories and the study by each student of some one industrial process along the lines in which he might be especially interested; for instance, in the manufacture of steel or of some other metallurgical process, in the manufacture and dyeing of textile fabrics, in the refining of oils, in the refining of sugar, in practical ceramics and in the manufacture of pharmaceutical products, etc., etc.

Of course, you will understand that these are merely suggestions, and can as yet be given only in a tentative way. That the proposition before us is a large one and will require a great deal of patient study, of course, I thoroughly appreciate.

With sincere regards,

Faithfully,

F. G. WIECHMANN

ST. LOUIS, MO., JUNE 18, 1910.

DR. F. W. FRERICHS,  
3828 Westminster Place, St. Louis, Mo.

DEAR SIR: I shall try to comply with your request, to express my opinion on the subject placed before the Committee on Chemical Engineering Education by the A. I. C. E.

I have carefully read your very interesting circular letter of February 4th, and will try to answer the questions therein put forth as well as it is possible for me, knowing but very little about the conditions now existing in American institutions of learning.

You ask in your letter to take as a basis for the discussion the course of chemical engineering submitted with your letter. I must confess that after having gone over the program of the subjects given in this course, I thought that a rather unfavorable example of chemical education in America had been chosen, having reasons to believe that the standard of chemical education of several other American universities and technical schools is by far higher than that at the university cited. On perusing the synopsis of chemical courses of this institution, I was confronted by the striking fact that the whole of the chemical education is in the hands of only three teachers, and most likely no one of the three has had any practical experience in any branch of chemical industry.

Considering the great diversity of the different branches of chemistry, it seems unlikely to me, to say the least, that effective teaching in all of these branches could be expected by such a small staff of teachers. In order to offer the opportunity to the student for thorough instruction in each one of the many courses, the combination of which constitutes a complete chemical engineering course, it seems evident that the teacher in each case should specialize in his branch. This is true of course for every line of study, but in our case more particularly so, especially for the instruction in chemical technology or industrial chemistry, where not only specialization on the part of the teacher is paramount, but where it is necessary also that his knowledge be based on practical experience.

Question No. 1.

Answer. No.

Question No. 2.

Answer. Yes and No. Four years should be a sufficient time for the education of a chemist, to make him fit to enter an industrial establishment, but all of these four years must be available for courses in chemistry and those other branches of knowledge necessary for the prospective chemical engineer. A sound general education must precede such a four years' course. This does not seem to be the practice followed in institutions

such as the one whose course is quoted, where a large part of the four years are devoted to topics of general educational character. In this connection, the question naturally arises, At what age should the special training of the student for chemical engineering begin? I do not feel qualified to make recommendations in this direction, not being sufficiently acquainted with the conditions in American grammar and high schools, but I venture to say that it can hardly be expected that a young man's general education could be rounded off before the age of 19 to 20 years. At this age, however, sufficient knowledge can have been acquired by the average student to make him fit to take up special studies.

It goes without saying that during these years of special studies opportunity must be given the student to follow courses of his own choice, not necessarily embodied in the program of the chemical engineering course. If this is done, the danger of unilateral professionalism can be satisfactorily met.

Question No. 3.

Answer. If a four years' course is made effective, as outlined in my answer to question 2, post-graduate work should not be considered an absolute necessity although it can but be beneficial. If, however, a four years' course comprises, besides chemistry, instruction in general educational topics, a post-graduate course of at least one or two years becomes a necessity.

Agreements should exist between institutions of the same grade, which should enable the student to follow a post-graduate course in the institution which offers the best opportunities for the particular line of work which he has chosen.

Question No. 4.

Answer. Not being acquainted with the character of post-graduate courses offered at American institutions, I do not feel qualified to express an opinion on this question.

Question No. 5.

Answer. Conditional for effective post-graduate courses is a thorough preparation for such work in the form of a course of chemical engineering which in itself should equip the average student with the necessary knowledge to enter chemical industry.

Question No. 6.

Answer. In answering this question, I can be guided by the example of the university chosen for comparison, and in this case I consider chemists from European polytechnic institutions by far better equipped even for American manufacturing plants than chemists having followed a course as such given at this university, even if they had taken one year's post-graduate work. However, I would not like to generalize and include among the chemists with European education those who come from all European universities, for the reason that in a great many of these latter institutions very little weight is given to the technical part of the chemist's education. Still, I believe that the average chemist with the European university education will be more efficient for research work in connection with chemical manufacturing than his brother from the American university quoted.

Question No. 7.

Answer. I do not feel qualified to pass criticism on the courses offered by the different American universities. I take the liberty, however, to submit a course which, in my opinion, would answer the purpose of turning out chemists ready to enter the practical field as chemical engineers. This plan is taken from the course prescribed for chemical engineers at the Swiss Polytechnic School in Zurich, and comprises  $3\frac{1}{2}$  years. It should, in my opinion, be increased to four years, thus providing more time for some of the important courses which suffer by the shortness of a  $3\frac{1}{2}$  year term. It must be remembered however, that this course presupposes a thorough general education.



	Hours per Week
<i>First Year—Winter Semester</i>	
Differential and Integral Calculus.....	7
General and Inorganic Chemistry.....	7
Analytical Chemistry.....	8
Analytical Chemical Laboratory.....	16
Mineralogy.....	5
<i>Summer Semester:</i>	
Physics.....	5
Organic Chemistry I (Aliphatic).....	7
Analytical Chemical Laboratory.....	16
Applied Mechanics and Mechanical Engineering.....	7
<i>Options:</i>	
Petrography.....	3
Applied Calculus.....	4
<i>Second Year—Winter Semester</i>	
Organic Chemistry II (Aromatic).....	3
Industrial Chemistry (Water, Salt, Acid).....	5
Fuel and Theory of Heat.....	3
Industrial Chemical Laboratory (Inorganic).....	16
Physics.....	5
Physical Laboratory.....	4
Applied Mechanics and Mechanical Engineering.....	7
<i>Options:</i>	
General Geology.....	4
Botany.....	2
Identification of Minerals.....	3
Microscopy I.....	4
<i>Summer Semester:</i>	
Organic Chemistry II (Aromatic).....	3
Industrial Chemical Laboratory (Organic).....	16
Physical Chemistry I.....	3
Industrial Chemistry (Alkalies, Chlorine, Phosphate).....	4
Technical Analysis.....	5
Engineering Laboratory.....	4
<i>Options:</i>	
Bacteriology.....	2
Botany II.....	2
Microscopy II.....	4
<i>Third Year—</i>	
Industrial Chemistry (Organic), Bleaching, Dyeing, Dyes.....	5
Metallurgy.....	2
Physical Chemistry II.....	3
Physical Chemistry Laboratory.....	4
Analytical Chemical Laboratory or Industrial Chemical Laboratory.....	16
Gas Analysis with Laboratory.....	1
Machines and Apparatus I.....	7
Industrial Hygiene.....	2
Electrochemistry.....	2
<i>Options:</i>	
Food Hygiene.....	1
Water Supplies.....	1
Bacteriological Laboratory, Elementary.....	4
Bacteriological Laboratory, Advanced.....	daily
Industrial Chemistry, Glass, Ceramics, Cement.....	3
Industrial Chemistry, principally Organic Dyestuffs.....	4
Industrial Chemistry, Organic Fats and Illuminants.....	3
Machines and Apparatus II.....	3
Analytical Chemical Laboratory or Industrial Chemical Laboratory.....	16
Explosives.....	1
Carbohydrates and Fermentation.....	2
Physical Chemistry, Advanced.....	2
Assaying.....	2
Hygiene of Heating, Ventilating and Lighting.....	2
Hygiene of Removal of Offal.....	2
Bacteriological Laboratory, Elementary.....	4
Bacteriological Laboratory, Advanced.....	daily
Human Anatomy and Physiology.....	2
Organic Electrochemistry.....	2
<i>Fourth Year—</i>	
Chemical Laboratory, Advanced.....	daily
Political Economy.....	2
<i>Options:</i>	
Food Analysis with Laboratory.....	4
Paper Manufacture.....	2
Spinning and Weaving.....	2
Business Law.....	4
Patents.....	1

I am fully aware of the fact that the few suggestions offered in the foregoing are a very superficial attempt toward the final solution of the great problem now before the institute. I am convinced, however, that a continued effort on the part of the members of the institute will eventually bring about the desired results of better efficiency of future generations of American chemical engineers.

Respectfully submitted,

I. VEILLON

DR. F. W. FRERICHS,

DEAR SIR: Replying to your letter of inquiry, I would make the following suggestions:

Place at the head of the industrial chemical department a man with practical experience in chemical technology.

By correspondence and coöperation with the principal chemical concerns and the judgment and experience of educators evolve a course in industrial chemistry. This should include a course in mathematics to and including a working knowledge of the calculus, two years each of French and German, one year of mechanical drawing with special attention to chemical machinery.

English throughout the course; equal attention to physics and chemistry throughout the course; one year of mineralogy and one year of economic geology.

If possible the student should be given practical work in a large chemical establishment after the Sophomore year.

The elaboration of these ideas would include the number of hours to be devoted to each feature of chemistry, physics, etc.

I do not believe in *thesis* work for the undergraduate student.

Very truly yours,

W. M. BOOTH.

From this correspondence and from oral discussions with members of the committee, it would seem that in their opinion even a successful four years' course at one of our good universities following a regular high school education is not sufficient to equip a student of chemistry satisfactorily to enter practical work.

As to the remedy, the opinions are divided, since it is proposed to require either a more advanced education in chemistry in the high schools or else post-graduate work after completion of the regular college course.

It seems to be the consensus of opinion that the post-graduate courses as offered now at American and many European universities are open to improvement if it is desired to fit post-graduate students for efficient research work in the chemical industries of the United States. In offering the subject for discussion in this meeting, it would seem to be of importance to bear in mind that the field of chemistry at the present day comprises specific knowledge in an almost infinite number of directions, and that in order to be successful it would seem to be imperative for a chemist to specialize and to concentrate his efforts on a small but well-defined part of the almost endless field of chemical research. This would not exclude the prospective manufacturing chemist from having a good general knowledge of the elements which form the basis of chemical engineering. On the contrary, he should have a good general knowledge of inorganic and organic chemistry and of physics and he should have perfectly assimilated these subjects so that it comes easy for him to think in terms of these sciences.

By making a large number of preparations he should have familiarized himself with the properties of the elements and their compounds, and should have a good knowledge of the methods of separating chemical compounds from mixtures and of the production of pure chemicals. Particularly should he be an expert in chemical analysis, even to that extent that he could criticize existing methods, devise new ones to fit new conditions, and he should be able to control the reliability of methods and to ascertain their limit of accuracy.

The graduate student should have a fair knowledge in ad-

vanced mathematics and its application, and be well trained in the drawing of machinery and structures.

He should have had manual training and be able to handle tools of the more important trades. His knowledge in languages should be such that he can read with ease professional publications in French and German languages and express himself clearly in English.

These studies, if pursued properly, would seem to fill an entire four years' course, and before they have been assimilated advanced work would seem to be of little benefit.

A chemist thus prepared may go into practice, but he leaves it to chance whether his progress will be rapid or slow. There may be instances where an intelligent manufacturer will lead him to apply his faculties to promising problems, but in most cases the first years will be wasted in futile efforts and costly experiments.

Quicker, certainly, and less costly experience in applying accumulated knowledge could be obtained by post-graduate work under the direction of good teachers at a well-equipped institution. But these institutions must be fitted to suit the particular requirements of American chemical industries, and the courses must be directed by teachers who are entirely at home among domestic manufacturing methods.

It has been pointed out by one member of your committee that the University of Zurich, Switzerland, has been particularly favored by having had for a long period of years two teachers, *viz.*, Guckum and Lunge, the former a successful manufacturer of coal-tar preparations, the other an expert in the soda industries, both of whom taught at the same time and were constantly in close contact with their respective industries.

Unfortunately it would seem impossible to duplicate these conditions in the United States. Expression has been given to the thought that no university could tempt a successful manufacturer in the United States to take up teaching, even if he had the ability to do so, and the average professor of industrial chemistry would hardly have the opportunity to obtain a full insight into the actual conditions of the chemical industries. What is published in hand-books of industrial chemistry to a large extent is hearsay and antiquated, and it is only natural that manufacturers are loath to divulge their experience for publication. The consequence is that the collecting and reporting professor of industrial chemistry is often teaching methods and processes long since abandoned and replaced by better ones.

What we must have for post-graduate work are producing teachers of industrial chemistry who, like Lunge, work ahead and do not follow the progress of the technical industries. Men of this kind will have information to offer to the manufacturers and in turn will obtain information upon which they are able to base the progress of their work.

To the places where such men teach, post-graduate students will flock and will be willing assistants for the work of their laboratories.

Some of the studies which might be taken up to advantage in a post-graduate course for chemical engineers are the following:

1. Exercises in making chemical preparations quantitatively—that means the making of chemical preparations, observing weights of raw materials used, time of reaction, concentration, pressures and temperatures most favorable for the production of chemical compounds, and the yield obtained. These exercises should be carried on in great variety and with great exactness, since they form the basis of most research work in chemical engineering.

2. Study of materials of construction for chemical apparatus, including metals, alloys, stoneware, cement, rubber, protal, wood, and others. These materials should be studied, not only

with reference to strain and workability, but also with reference to action of various chemicals upon the materials.

3. Study of construction of machinery and apparatus. This should include a study of the limitation of materials in their application for making apparatus and also the preservation of apparatus from destructive influences.

4. Measuring apparatus and methods of measuring.

5. Study of the generation of steam: types of boilers and boiler furnaces, boiler feed water, purification of same, fuels, methods of making tests for efficiency, firing with coal, oil or gas, calculation of cost.

6. Water supply.

7. Study of generation of power, steam engine, water wheels, electric motors, transmission of power.

8. Construction of furnaces, pyrometry, materials for furnaces, construction, repairing same, construction of chimneys, fuels for furnaces, efficiency, calculation of cost.

9. Study of evaporation of liquids and solutions under high pressure, under atmospheric pressure and *in vacuo*, concentrating solutions, calculation of cost.

10. Construction of drying plants, theory of drying, drying *in vacuo*, collecting evaporated solvents.

11. Theory of distillation and construction of stills, rectification, dephlegmation condensation.

12. Theory of saturation, extraction, and absorption.

13. Study of evaporation of solids, resublimation.

14. Theory of crystallization, crystallization in motion and *in vacuo*.

15. Methods of treating solids with liquids.

Methods of treating solids with gases.

Methods of treating liquids with gases.

16. Methods for purifying solids, liquids, or gases.

17. Grinding and disintegration machinery, separating and mixing machinery.

18. Handling of solids in large quantities.

Handling of liquids in large quantities.

Handling of gases in large quantities.

19. Buildings and structures for chemical plants.

20. Packages and materials for same.

21. Handling and disposition of labor and prevention of accidents.

Liability insurance.

Accident insurance.

Regulation of wages.

22. Sampling and testing chemicals.

23. Controlling the manufacture by logs.

Factory bookkeeping and calculations.

24. Patent law, tariff law, corporation law, contracting.

25. Discussion of special industries.

It is true, many practical problems *cannot* be carried out in a laboratory on a small scale, and therefore *cannot* be an object of study in a post-graduate course. But a very great number of processes *can* be worked out in the laboratory and it would seem that in connection with these the theoretical part of industrial chemistry could be worked out in a satisfactory manner. In order to do this there must be at least one teacher of industrial chemistry and at least one institute which will carry out the work.

Our friend, Dr. Baekeland, said recently in his address at Pittsburg, that the principal object in a research laboratory is the research chemist himself. I think he is right. But it is believed that it will be a long time before the universities without the assistance of practical manufacturers can produce such a man. In my opinion, the A. I. C. E. could be of great assistance in bringing this about. If a university of high standing would undertake to establish a post-graduate course for chemical engineering, the A. I. C. E. might offer the assistance of a committee from among its members, to act in a consulting capacity

to the faculty and to help in this manner, to originate an efficient course. But it would seem necessary that the professor of industrial chemistry to whom the work of post-graduate students is entrusted devote his entire time to this work and be not burdened with work in undergraduate departments. He should have a well-equipped laboratory and a staff of the best assistants at his disposal, since the field of research is large and the detail work, particularly in the beginning, would seem overwhelming. As to the duration of such a course, it is thought that two years are sufficient if only well-prepared students are entered. Upon the termination, an appropriate degree might be conferred which no doubt would be highly treasured by the possessor.

#### COMMITTEE ON CHEMICAL ENGINEERING EDUCATION.

F. W. FRERICHS, *Chairman*.

#### PRESIDENT McKENNA:

This painstaking and valuable report will be printed in a Bulletin in anticipation of the regular Transactions. The members of the institute will be asked to send to the Secretary their opinions on this subject. These will be edited by the Committee on Chemical Engineering Education, and will, together with this report, form the basis of a progress report at least at the annual meeting. If there is anything of importance that members wish to put forward at this time—some important view—it would be well, of course, for us to have it.

#### SECRETARY OLSEN:

I feel in the first place that the institute is undertaking a very important work. I am ready to admit that the conditions in American colleges and American universities are in many cases deplorable. I think there is no question of it. There are certain influences at work at present to improve and change those conditions, and I am glad to see this institute entering the field. There are too many colleges in the country poorly equipped and with very little endowment. Why, in one State they passed a law that a college should not grant degrees unless they had an endowment. The law as at first proposed was that that endowment should be—half a million? No, \$25,000 was enough to make a college. After the legislators had discussed the matter, they decided that it was too high, and brought it down to \$5000. As Dr. Butrick has said, any preacher can give his note for \$5000, and establish a college and give degrees. I say that public opinion should stamp out such institutions, and place American education on as good a basis as American industries generally are, and root out a lot of those poorly equipped institutions which are in the field giving degrees.

After having said that, and saying that we ought to educate public sentiment for thorough, sound, and broad education (and we can begin a lot lower than Dr. Frerichs has suggested and do good work), I want to say a few words with reference to the typical courses which have been given. You will have noticed the great difference between the three propositions. The last one, giving the course at Zurich, included a long list of technical subjects covering all branches of applied chemistry. That was in Europe. The other suggestions are much simpler. Our practice differs from that in European countries in education, as well as in industry. When American capitalists have built a railroad through the country, they have in many cases thrown the ties down on the bare ground, spiked down the rails and started running trains. That's cheap construction. After they have constructed it in that way they begin to gather in the earnings. Then they proceed to raise the track here, place a bridge there, straighten the track and put in ballast, and to improve the equipment, and after a few years, using the earnings, the road will be in pretty fair condition. In Europe how do they do it? Their capitalization per mile is very heavy, because they build a railroad complete in the beginning. Now the education given in that course at Zurich was designed to be complete right at the start; it is supposed to turn out a man who

knows all about vacuum drying right from the school. We do not do that in America. How do we do? In America we say, give a man a broad, general education, give him the principles of his science, drill him until he knows the broad fundamental principles, and then, if he goes into Dr. Frerichs' laboratory, he will soon learn how to distill ammonia. We trust him to pick things up as he goes along, and go upon the plan of not giving specialties in college. I received my technical training at the Johns Hopkins University. They said: "We will not teach qualitative analysis very thoroughly; we will teach you the properties of chromium until you know chromium—know it so that you could find it under any and all conditions." So we in America have gone at the problem of education from that standpoint. Give the students a broad general training in the principles of the sciences—theory, if you choose to call it so. We have said that if he has the principles of chemistry and engineering, if he has his mathematics, his German, and his French, so that he can read the literature, he will get the applications. Now the question is, Is that the right principle to start out on? I would like an expression of opinion of this institute as to whether that is the way to proceed.

#### MR. BAKER:

I do not want to throw cold water on any steps which may be taken to turn out industrial chemists, but I do not think it is possible to turn out a full-fledged industrial chemist. The conditions in the factory are entirely different, if not diametrically opposite to those in the laboratory. In the laboratory the work is done under ideal conditions, and the least important factor is economy. In the industrial plant the most important factor is the economical one, because an industrial plant is run to make money and not to demonstrate a chemical theory. Another important factor is that of the physical conditions he must contend with, and does not meet in the laboratory—the "cussedness of inanimate things"—I do not know a better way in which to express it. Some one has aptly said that to gain an education is to cultivate an attitude of mind, which I take to mean, to learn how to look at things. The best chemist is not the man who works all hours of the day working out a problem given in a book, nor a man who burns the midnight oil, but the man who looks into things—the man of an investigative turn of mind—the one whom you would term a crank—one with the spirit of the boy who cut the head of the drum to find out what made the noise.

#### PRESIDENT McKENNA:

The institution named in the committee's report was taken only by chance, and if we were to take the statements made and opinions expressed upon the course in that institution too literally, it would appear as if it were very unfairly treated. That is not the meaning, I feel sure, of such an inquiry. It was referred to only as a typical institution of medium grade.

#### AMERICAN ELECTROCHEMICAL SOCIETY.

Chicago Meeting, October 13 to 15, 1910.

Headquarters Congress Hotel.

WEDNESDAY, OCTOBER 12TH.

6 P.M. Registration.

THURSDAY, OCTOBER 13TH.

9 A.M. Meeting of Directors.

10–12 A.M. Reading of papers at Florentine Room, Congress Hotel. Thursday afternoon, four alternative excursions.

- (1) Fisk St. Power House of the Commonwealth, Edison Co.
- (2) Western Electric Co. Works. (3) Automatic Telephone Co. Works, Market St. Transformer and Storage Battery Station of Commonwealth Edison Co., and the Demonstration Installation of the Hoskins Mfg. Co. (4) The Union Stock Yards and the Plants of Swift and Company, Armour and Company and Morris and Company.



## FRIDAY, OCTOBER 14TH.

9-12 A.M. Reading of papers at Florentine Room, Congress Hotel. Friday afternoon, three alternative excursions.

(1) Illinois Steel Co., South Chicago Works. (2) Gary Steel Works. (3) Sears, Roebuck and Co., with a complimentary luncheon for visitors.

Friday evening, dinner at Congress Hotel.

## SATURDAY, OCTOBER 15TH.

9-12 A.M. Reading of papers at Kent Chemical Laboratory, University of Chicago, followed by inspection of laboratories and museums and a luncheon at the University Commons. Afternoon, two alternative excursions.

(1) The Lockport Power House and the Drainage Canal. (2) The Field Columbian Museum.

For the entertainment of visiting ladies an automobile trip to Hull House, The Juvenile Court, Mark White Square and the Stock Yards, with a luncheon at Hull House is planned for Thursday. On Friday morning visits will be made to Marshall Field's Retail Store and The Art Institute. Sears, Roebuck and Co. will entertain both ladies and gentlemen at luncheon and later show visitors through their establishment. Ladies are especially invited to participate in the luncheon at the University on Saturday. In the afternoon they may visit either the Field Museum or the Drainage Canal and Lockport Power House.

General Committee—Herbert N. McCoy, *Chairman*; Arba B. Marvin, *Secretary*. Entertainment—Harry McCormack, *Chairman*. Excursions—F. T. Snyder, *Chairman*. Press—H. T. Matthew, *Chairman*. Ladies—Mrs. W. D. Richardson, *Chairman*.

## PAPERS.

## THURSDAY, OCTOBER 13TH.

10.00 a. m. Reading and Discussion of Papers, Florentine Room, Congress Hotel: "Method for Determining Thermal Conductivity," Carl Hering.

"The Electric Furnace and Its Application," Marcus Ruthenburg.

"Electrolytic Method of Producing Metals," John W. Beckman.

"Reduction of Tin Dross in the Electric Furnace," R. S. Wile.

"Notes on Tribo-Luminescence," W. S. Andrews.

"The Proximate Constituents of the Chemical Elements with Reference to Radioactivity and Electrons," Gustavus D. Hinrichs.

## FRIDAY, OCTOBER 14TH.

9.00 a. m. Reading and Discussion of Papers, Florentine Room, Congress Hotel: "Electrochemical Preparation of Calcium," Prof. A. R. Johnson.

"Efficiency in the Electrolytic Preparation of Calcium," Francis C. Frary, Henry R. Bicknell and Carl A. Tronson.

"Electrochemistry of Polonium and Other Radioactive Elements," Prof. A. R. Johnson.

"The Present Status of Ozone," R. D. Small.

"The Evolution of the Lead Storage Battery," Pedro G. Salom.

"A New Secondary Cell," W. S. Block.

"The Self Discharge of Plante and Faure Storage Batteries," Prof. O. W. Brown and W. G. Bowers.

"Corrosion of Metallic Food Containers—Causes and Prevention," Dr. Edward Gudeman.

"Electrolytic Corrosion of Various Metallic Anodes in a Liquid Ammonia Solution, Ammonium Trinitride," A. W. Browne and E. Holmes and J. S. King, Jr.

"Electrolysis of Solutions of Ammonium Trinitride and of Potassium Amide in Liquid Ammonia, A. W. Browne and M. E. Holmes.

"On the Electrolysis of Some Cyanides," H. E. Patten and W. R. Mott.

## SATURDAY, OCTOBER 15TH.

9.00 a. m. Reading and Discussion of Papers, Room 20, Kent Chemical Laboratory, University of Chicago.

"Application of Electrostatic Separation to Ore Dressing," F. S. MacGregor.

"The Isolation of an Ion and a Precision Measurement of Its Charge," Prof. Robert A. Milliken.

"Phenomenon of Crystallization through Membranes," Dr. J. H. Walton, Jr.

"On the Relative Basicity of the Metals as Shown by their Power to Replace One Another in Chemical Compounds," Dr. L. Kahlenberg.

"On the Effect of Water in Causing Chemical Reactions," Dr. David Klein.

"The Physical and Magnetic Hardness of Some Electrolytic Iron Alloys," James Aston.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

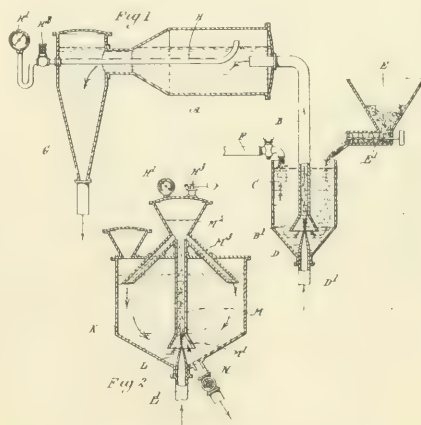
Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

966,389. Wet Process for the Treatment of Ores. H. T.

DURANT, *et al.*, patented August 2, 1910.

This invention relates to wet processes for the treatment of metalliferous ores or compounds particularly of zinc, and more particularly to processes in which ores containing zinc oxide are treated with a solution of sulfurous acid so as to obtain a solution of bisulfite of zinc.

Hitherto it has been proposed to effect the agitation of the ore or compound with water or other liquid in an apparatus comprising a tank having a pipe open at both ends and arranged vertically therein, and means for introducing at the foot of the pipe a lifting medium such as compressed air for raising the liquid contents of the tank up through the aforesaid pipe thereby promoting a circulation of the said contents. Apparatus of the general type in which a jet or injector is used

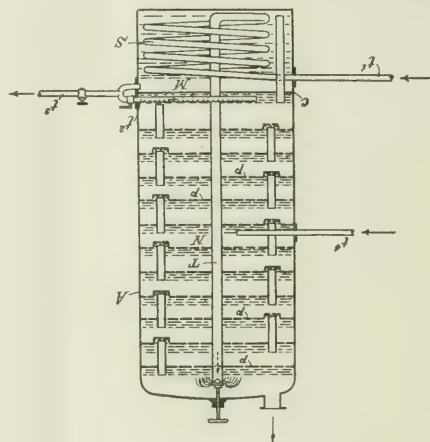


to cause circulation of a mixture of ore and liquid will be hereinafter referred to as an injector agitator.

According to this invention an injector agitator is supplied with a medium which does not merely promote circulation of the contents of the apparatus but has a chemical effect upon the said contents. The aforesaid medium may be in the form of a soluble gas, in which case it will become absorbed by the liquid in the agitating apparatus, or it may be already in solution when introduced. For example, when treating zinc ores suspended in water with sulfur dioxide, the sulfur dioxide derived from the roasting of the sulfid ore, or otherwise, may be introduced directly at the foot of the vertical pipe in the injector agitator containing the roasted ore in suspension in water; or the gas may be first absorbed by water and the dilute sulfurous acid solution so obtained may be injected under pressure up the aforesaid pipe. In the former case the gas will soon become absorbed by the water forming dilute sulfurous acid and in either case the dilute acid solution will exert a chemical action on the roasted ore in the known manner.

Another example of the application of this invention to the zinc bisulfite process already referred to resides in the use of steam or hot gases in an injector agitator for the conversion of soluble bisulfite of zinc into the insoluble monosulfite. The steam or hot gas may be introduced at the foot of the pipe in an injector agitator and a reduced pressure may be maintained on the surface of the bisulfite of zinc solution, the result being the heating and agitation of the contents of the apparatus and the conversion of the bisulfite of zinc into the monosulfite with evolution of sulfur dioxide. Zinc or other ores may be similarly treated with other appropriate chemically active gases, either free or in solution. Ores containing zinc or copper may be, for example, treated in the manner hereinbefore described with ammonia either in the hydrated or gaseous form. The soluble gas or gases, or the solution thereof may be used in substitution for the mere lifting medium hitherto employed in the injector agitator in addition thereto.

The accompanying illustration shows the apparatus in which the process is carried out.



**967,105. Process for the Separation of Gaseous Mixtures into their Elements.** GEORGES CLAUDE, *et al.* Patented Aug. 9, 1910

This is a process for the separation of oxygen in any desired degree of purity from atmospheric air by means of liquefaction and evaporation.

This process is based upon the fact that in order to transform liquid air into very pure liquid oxygen by the progressive evaporation of the nitrogen and the simultaneous liquefaction of a corresponding quantity of oxygen, it is sufficient to bring nearly pure cold gaseous oxygen into contact with liquid air in any manner, as for instance by causing the gaseous oxygen to pass in bubbles through the liquid air. By evaporating the liquid oxygen which is obtained we obtain a quantity of gaseous oxygen greater than that used, and if the apparatus is suitably devised, greater than the quantity of oxygen previously contained in the liquid air used, and this entire excess may be furnished by the atmosphere. This evaporation of the oxygen is made use of in our invention. It is effected by forcing cold air under suitable pressure into a tubular vessel or into a coil immersed in liquid oxygen. The evaporation of oxygen will thus cause the condensation of a substantially equivalent quantity of air under pressure, and we thus obtain a quantity of liquid air nearly equal to that at the start which, in its turn, is separated into pure oxygen by repeating the same operations.

In order to give this method its highest practical value, it is essential that the oxygen gas be utilized as completely as possible; the simple passage in bubbles through the liquid mass would yield poor results, for it is evident that the gas at its outcome from the liquid holding a large quantity of oxygen

and the loss would be greater than the gain. It is therefore of importance that this passage of the oxygen gas through the liquid air be carried out in a particular manner, for instance, by supplying the liquid air to be converted into oxygen at the upper part of a column provided with baffle plates or other suitable device and by supplying the gaseous oxygen at the lower end of the column, so that the gas travels through the successive chambers and issues from the column at the point of supply of the liquid air.

It is well known that if the liquid air at its formation contains, like the atmospheric air, about 21 per cent. of oxygen, the gas at its issue contains only about 6 or 7 per cent. of oxygen. If it be necessary to retain these quantities, it is possible to provide the column with an extension, at the end of which

there is fed liquid air containing less than 21 per cent. of oxygen. The losses in cold in the column can be compensated for either by the introduction of liquid air obtained from an auxiliary source or by the expansion of the air to be liquefied, compressed for this object.

The figure shows an apparatus in which the process is carried out.

**967,996. Method of Extracting or Eliminating Sulfur, Phosphorus, and Other Impurities from Coal Ore, Etc.** LELAND L. SUMMERS. Patented August 23, 1910.

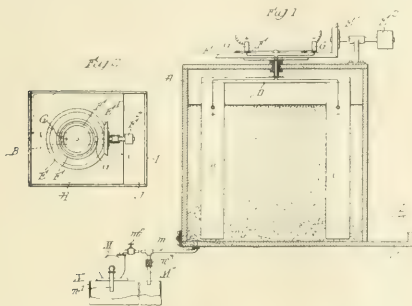
This invention relates to a method of eliminating those impurities from coal, ore, etc., which are detrimental and troublesome in the manufacture of iron and steel, and the object is to provide a simple and efficient method of removing such impurities from the raw material used. Thus, according to this method, in the case of coal to be coked, the sulfur and phosphorus are removed from the coal before the same is charged into the coking appliances, and in the case of ore, the impurities are removed previous to charging the ore into the blast furnace or other refining apparatus.

In general terms, the invention consists in providing a method by which the sulfur and phosphorus is chemically acted upon and its form of occurrence changed so that it may be removed as a different chemical compound.

The method is based essentially upon the fact that upon the passage of an electric current in a suitable electrolyte, electrolytic decomposition will result. According to this method as practiced, the coal or ore to be electrolyzed is preferably in a finely subdivided form and is submerged in the electrolyte,

so that upon revolving the electrodes *B* and *C* a continual agitation of the substance is in contact with the products of electrolysis.

In the use of the apparatus illustrated in the practice of the process, the rotation of the electrodes *B* and *C* in addition to agitating the electrolyte, will cause a portion of the material



treated to first be subjected to the acid and oxidizing reaction and immediately afterward to be subjected to the alkaline and reducing action. Thus, the bisulfid and monosulfid of iron in the vicinity of the anode will be violently reacted upon, the bisulfid being oxidized and the monosulfid being decomposed as before mentioned. Immediately after this action, the same particles will be subjected to the action of the sodium hydroxid liberated by the cathode, this being caused by the rotation of the electrodes so that the cathode and anode are changing places. The rate of rotation is determined by the strength of the reaction desired.

**968,954. Metallurgical Furnace.** JOHN E. JONES. Patented August 30, 1910.

This invention relates particularly to furnaces for treating or sintering ores, flue dust, and other comminuted materials, preliminary to further treatment in a blast furnace or other reduction apparatus.

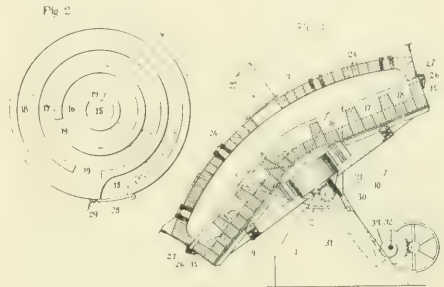
In processes of obtaining metals such as iron, zinc, copper and the like now in common use, large quantities of dust and material rich in metal, but too fine to be smelted, are obtained. Also various metals occur in the form, or ores which are so fine as to require sintering or nodulizing prior to being reduced.

This invention has for its object the production of a furnace for the treatment of such materials whereby ores can be de-

furnace wherein the finely divided material to be treated is fed into the center of a rotary inclined hearth provided with a tortuous path, such as a spiral, but more preferably with communicating grooves surrounding each other, the material dropping from one groove into the adjacent groove by gravity, as the hearth rotates, and in conjunction therewith, a relatively stationary hood is provided whereby to form a heating chamber enclosing the hearth. In conjunction therewith means are provided for applying heat to the interior of the furnace, and preferably, the heating means are so disposed as to direct a flame directly on the material undergoing treatment.

The invention further comprises a furnace of the general character above described wherein the hearth will be mechanically driven, and also mounted in such manner that the inclination of the hearth can be adjusted as may be desired without interfering with the arrangements for heating the interior, or with the driving means.

In the specific embodiment of the invention herein shown, the grooved hearth is made in the general form of a cone, that is to say, the grooves or channels containing the material being disposed in different plane, and the hearth itself being mounted on trunnions whose axis coincides with the axis of the driving

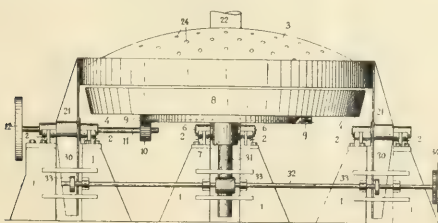


shaft, whereby permitting the hearth, together with the table, to be swung on the trunnions to any desired angle and still maintain the driving connection.

**968,760. Obtaining Petroleum Products.** HERMAN FRASCH, of New York, N. Y. Patented August 30, 1910.

This invention relates to the production of useful products from a certain kind of petroleum which is characterized as hereinafter set forth and is herein termed Coalinga oil, or Coalinga petroleum for convenience of reference. It is found in the neighborhood of the town of Coalinga, in the county of Fresno, and State of California. Ordinarily, on distilling petroleum and testing the gravity of successive samples of the distillate as it runs from the tail pipe of the condenser, it will be found that the distillate becomes gradually denser and less volatile as the temperature in the still rises. In other words, the boiling points and densities of the hydrocarbons of petroleum usually increase together; and the greater the density of a hydrocarbon from a given crude petroleum, the higher boiling point may it ordinarily be expected to have. The patentee claims to have discovered in the Coalinga petroleum an extraordinary exception to this general rule; that is to say, he claims to have discovered in Coalinga petroleum an oil which, on distillation, may at intervals exhibit retrogressions of density in the distillate, while the volatility of the latter continues to decrease. Coalinga oil, therefore, contains hydrocarbons which are specifically heavier than others of higher boiling point in admixture therewith.

The still *a* is supported and heated in any suitable way. The



sulfurized, and also formed into nodules by partial fusion, and thereby rendered capable of economic treatment without undue loss in the blast furnace.

According to this invention, the patentee has provided a



column *b* is shown as made in sections, and has a perforated or reticulated floor plate, *c*, at the bottom of each section, which floor plate supports the finely divided solid material *d*, say, two feet of gravel for each section. The gravel in the two lower sections may be such as to pass through a sieve of two meshes to a linear inch and to be arrested by one of three meshes to the linear inch; that in the upper sections may be a little smaller, say, gravel which will pass through the last-mentioned sieve and be arrested by one of four meshes to the linear inch. Either size of gravel could be used in all the sections, but it is considered better to have the gravel of the lower sections a little larger on account of the larger volume of liquid of condensation therein.

Below each floor plate, *c*, is a collar, *e*, for directing the down-flowing liquid of condensation from the walls of the column toward the axis thereof.

The column *b* is covered with a coating, *f*, of an inch and a half of asbestos cement.

The vapor pipe *g* leads from the top of the column *b* to the condenser, of known or suitable construction. Branch pipes, *h*, with valves, *i*, therein are shown connecting with the space

as customary. As the mixed vapors rise through the tall column of finely divided solid material, they become partially condensed to a liquid, which immediately commences to descend toward the still *a*, covering the pieces, *d*, of solid material in its passage. The cooling of the air, modified by the asbestos jacket *f*, gives a gradual fall of temperature in the column from the bottom upward, and keeps the solid pieces effectively covered with coherent coatings of the downflowing liquid, the supply of which is being constantly renewed by condensation at points above.

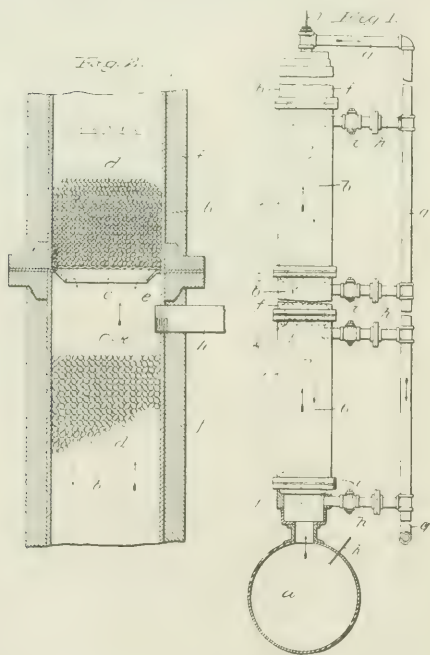
Since the cooling takes place at the outside of the column, the temperature at outside points is naturally lower than it is at interior points at the same level; and the tendency, therefore, is for the flow of condensate to be greater at the outside than in interior parts of the column. The collars *e* between overlying and underlying portions of the column counteract this tendency by deflecting the current of condensate from the outside of each overlying portion horizontally toward the interior parts of each underlying portion. A more uniform distribution of condensate over the solid matter of the underlying portion of the column is thus effected.

At any given point in the column the rising vapors, which consist of a mixture of hydrocarbons of different boiling points, are meeting and coming into intimate contact with the descending liquid, which consists likewise of a mixture of hydrocarbons of different boiling points. Of these liquid hydrocarbons, some are of lower and some of higher boiling points than a part at least of the vaporized hydrocarbons, which meet them in any particular point. There are consequently repeated fractional condensations from the vapors, and fractional re-evaporations from the liquid of condensation, until the well rectified vapors escape by the vapor pipe *g*.

The fire under the still *a* may be so regulated as to distil off about 2 per cent. per hour of the charge placed in the still *a* at the beginning of the run. As distillation proceeds, the temperature in the still *a* and column *b* rises; the density of the distillate at the tail pipe of the condenser for the most part increases and the volatility of said distillate steadily diminishes, but at certain periods said density gradually diminishes while said volatility continues to decrease. Such a retrogression in density of distillate takes place before the thermometer *j* reaches 260° F.; and when this temperature is reached, the distillate receiver may be changed, so that distillate next collects in the new receptacle.

The distillation being continued, the density of distillate gradually increases with the rise of the distilling temperature until another retrogression of such density takes place which occurs before the temperature at the top of the column reaches 320° F. When this temperature is attained the distillate receiver may be again changed. The distillation may then be continued until the temperature at the top of the column reaches 400° F., when the top section may be cut out by opening the valve *i* in topmost branch pipe *h*, so that the vapors pass through it to the vapor pipe *g*. The distillation may then be continued until the temperature at the top of the third section reaches 485° F.

It could be continued longer, or stopped earlier. The residuum is then discharged from the still *a* and column *b*, in preparation for another run. By the distillation described, three fractions of Coalinga petroleum will have been obtained, namely (1) the fraction collected before 260° F. is reached; (2) the fraction collected before 260° F. and 320° F.; and (3) the fraction collected between 320° F. and, say, 485° F., more or less. The first contains the benzene and toluene of the crude oil, the second the xylene and some of the mesitylene, and the third the rest of the mesitylene and the naphthalene. This separation is not expected to be perfect, however. In making it as described, the hydrocarbons which come over near



below each column section, for enabling the vapors to pass to the condenser direct from the still *a* or after passing through any one or more of the column sections as may be desired.

A thermometer, *j*, is placed in the top of the column *b* to indicate the temperature of the vapors entering the vapor pipe *g*; and there may be thermometers at the points *k*.

This distilling and rectifying apparatus being at hand, the still is supplied with the crude Coalinga petroleum; and the temperature of the still and contents are raised to the distilling point. After a time the vapors pass over by the pipe *g* to the condenser, where they are condensed to a liquid, which runs out of the tail pipe into the customary box, which is so arranged that the flow can be observed and samples taken for testing,

the beginnings of the respective retrogressions would not be collected apart from those which come over near the endings thereof.

Each of the so obtained fractions is distilled by itself with rectification in the column *b*, or with other rectification able to effect the aforesaid retrogressions of density of distillate contemporaneously with continued decrease of volatility; and the hydrocarbons which come over near the beginnings of the respective retrogressions are collected apart from those which come over near the endings thereof.

The inventor is Herman Frasch, of New York, N. Y.

## INDUSTRIAL AND TRADE NOTES.

### GERMAN RESINITE COMPOUND.

(From Consul Thomas H. Norton, Chemnitz, Germany.)

The previous report on the new German material, resinite, which appeared in Consular and Trade Reports for May 7, 1910, has elicited so many inquiries regarding its manufacture and uses that the following additional facts are presented:

The essential feature in the technical method now used to produce resinite is the condensation of phenol and formaldehyde. By condensation is understood the union of two or more molecules of organic compounds, with elimination of one or more molecules of water. The operation is, in this last respect, comparable to that which occurs when an acid and a metallic hydroxide react to form a salt and water is liberated. In most organic compounds condensation is effected by bringing them in contact with other substances which have an affinity for water and thus favor the reaction.

The condensing agents used by the inventors of resinite are certain mineral salts, such as sodium sulphite, ammonium sulphite, tertiary sodium phosphate, sodium acetate, and a few others. All of these salts are neutral or exert a feeble alkaline reaction. The use of these simple agents constitutes the principal peculiarity of the patented process, as contrasted with the employment of acids or alkalis, methods which have been practised for many years in effecting synthetic condensations similar to those giving rise to resinite. The inventors claim that by the use of the milder, less energetic agents the ensuing reaction is under more perfect control than when acids are employed, and that it is possible to isolate certain valuable intermediary products through the ease with which the operation can be interrupted at any point. The condensing agents may properly be considered as catalytic substances.

In actual manufacture phenol (carbolic acid) is mixed with an aqueous solution of formaldehyde (40 per cent.) and heated, after the addition of one of the salts mentioned above. The product is a yellowish, mobile liquid, which is termed resinite-A. It is admirably adapted for impregnating wood, paper, and other porous materials, and thereby rendering them waterproof.

If resinite-A be freed from the water present by distillation, a residual product is secured, termed resinite-B. The properties of this substance vary, according to the rapidity of the distillation and the prevailing temperature. Normally it is hard under ordinary conditions, but becomes plastic as the temperature rises. If it be now heated for a long time at 80° C., and then the temperature be raised to 200° C., resinite, properly so called, is the result—a perfectly solid, infusible, insoluble substance, exceedingly resistant against both acids and alkalis. Ordinarily exceedingly resistant against both acids and alkalis. Ordinarily it is of a ruby-red or purple tint. The color is yellow if ammonium salts have been used as condensing agents. It is transparent, or translucent, highly lustrous, and shows a conchoidal fracture. The ease with which it can be colored through

the application of anilin dyes to the surface, or throughout the entire mass, renders it of value for a multitude of technical purposes. It is used for the heads of hat pins, for chandeliers, for decorating signs, etc. It can be ground, turned, polished, etc., but as it is somewhat brittle, its use in this form is subject to certain limitations.

Resinite can be modified during the process of formation by the addition of a variety of substances, such as talcum, infusorial earth, starch, etc. The resultant product is no longer transparent, but it has acquired the important property of elasticity, and can now be easily worked.

For certain purposes, for example, in forming buttons from resinite, the long-continued heating, for at least two hours, as involved in the process as outlined above, is practically out of the question. In such cases treatment with hydrochloric acid is employed. If resinite containing 20-30 per cent. starch be warmed with dilute hydrochloric acid, a viscous product is obtained which can be poured into molds, rolled into sheets, etc. The acid employed for this "tempering" is easily removed by washing with a dilute soda solution. The solidified mass is no longer brittle, but soft and easily worked upon the lathe or with various tools. When poured into molds very clear, sharply defined results are obtained.

Numerous difficulties were encountered in coloring masses of resinite, as the various anilin dyes undergo striking changes in the course of the final operation. It is now possible, however, to secure resinite in any color except white and gradations of white.

In its various modifications resinite shows valuable technical properties, resembling those of glass or celluloid in some forms, while in others it approaches ebonite, horn, vegetable ivory, or Japanese lacquer. It has but little in common with natural or artificial resins. The inventors propose the general name of "resit" for resinite-B and similar compounds and "resol" for resinite-A and analogous substances. (The address of the German manufacturer of resinite is on file in the Bureau of Manufactures.)

It is worthy of note that an American invention closely corresponds with resinite in many of its properties and applications. It is of wide use in the United States as an insulating material in electric installations and for other purposes. One of the largest chemical companies in Germany has recently begun manufacturing under its patents for the European trade. This substance is called "bakelite." The essential features of the American invention consist in the use of bases as condensation agents and in the combined action of heat and high pressure to effect the final change into the hard, insoluble modification. There would appear to be a certain measure of conflict between the claims of the two patentees.

The exact chemical composition of these materials has not yet been established on account of the chemical inertness of the substances. The analytic results harmonize with the empirical formula  $C_{43}H_{58}O_7$ .

### GERMAN POTASH PRICES.

THE SYNDICATE FIXES QUOTATIONS TO DOMESTIC CONSUMERS.

Consul Talbot J. Albert writes from Brunswick that negotiations have been in progress for some time between the new potash syndicate and the associations belonging to the organized German agriculture as to the prices for raw and fertilizing salts to be furnished for the use of the domestic agriculture.

An agreement has been reached and the following are the prices per double centner of 220 pounds for raw salts, based upon the maximum prices established by the potassium law just enacted (mark = 23.8 cents):

	Raw salt.	Now.	Formerly.
Karnallit:		Marks.	Marks.
9 per cent. potassium.....		0.765	
10 per cent. potassium.....		0.85	0.90
11 per cent. potassium.....		0.935	
Hartsalz and sylvanit:			
12 per cent. potassium.....		1.20	
13 per cent. potassium.....		1.30	
14 per cent. potassium.....		1.40	425
15 per cent. potassium.....		1.50	

Formerly, when sylvanit contained more than 13 per cent. potassium, there was an addition of 10 pfennigs (2.3 cents) for each half per cent. potassium, unless the customer ordered expressly lower that is to say, normal per cent. goods. In the case of hard salts formerly an excess of 12.4 per cent. potassium was not taken into consideration in the reckoning. The syndicate now seeks, in consequence of the reduction of prices for normal marks which has to be made under the law, to equalize prices partly by imposing on orders for salts having a larger percentage potassium than the normal an additional sum to that formerly charged. No just objection can be made against this method by consumers, as it enables the reasonable employment of the better works.

#### PRICES OF FERTILIZING SALTS.

The prices of manure salts, which also show greater differentiation, are as follows, per 220 pounds: Containing 20 per cent.  $K_2O$ , 2.80 marks; 21 per cent., 2.94 marks; 22 per cent., 3.08 marks; 30 per cent., 4.35 marks; 31 per cent., 4.495 marks; 32 per cent., 4.64 marks; 40 per cent., 6.20 marks; 41 per cent., 6.355 marks; 42 per cent., 6.51 marks.

There is an additional charge to all prices of 0.04 mark for transport from the works to the shipping station; for mixing with  $2\frac{1}{2}$  per cent. turf mull the price is increased 10 pfennigs. All prices are understood to be for 100 kilos (220 pounds), with  $2\frac{1}{2}$  per cent. discount at the works. For 100 kilo sacks for karnallit, kainit-hartsalz, and sylvanit there is an additional charge of 40 pfennigs per sack and for manure salt sacks 47 pfennigs.

#### REBATES—EXPORT PRICES NOT FIXED.

The question of rebates has been regulated in the following way: In case of the annual purchase of 10-500 double centners of kali (potassium salts) the discount for karnallit containing 9-11 per cent. potassium is 3 marks; for kainit-hartsalz, and karnallit containing 12-15 per cent. potassium, 5 marks; for manure salts containing 20-22 per cent. potassium, 8 marks; containing 30-32 per cent., 12 marks; and 40-42 per cent., 15 marks. In case of the annual purchase of 501-2,000 double centners the rebate rates have the following sequence, namely, 4, 7, 10, 14, and 19 marks, and in case of the purchase of more than 2,000 double centners of salts the sequence is 6, 9, 12, 17, and 23 marks.

In order to secure the second grade of rebates on 501 double centners of salts there must be an annual purchase of about 40 carloads of kainit-hartsalz or about 12-13 carloads of manure salts containing 40 per cent. of potassium, or about 30 carloads of kainit and 3-4 carloads of manure salts containing 40 per cent. of potassium, equivalent to 100 double centners. What is specially to be noted is that by these rebates no commission or allowance of any kind, directly or indirectly, is to be made to the consumer.

As has been said, these prices are for the German agriculturists. No prices have as yet been published for the American importers. The difference which arose some time since between the old syndicate and the mines outside of the same who had contracts with American companies have not yet been settled. There are continuous negotiations between the new syndicate and the outside parties, but no result has been reached. The foregoing prices will at least be valuable to show whether any

discrimination is made in the future against the American farmer.

#### WATER PURIFIED BY OZONE.

(From Consul William Dulany Hunter, Nice, France.)

As the water used here for drinking and other purposes was considered to be unwholesome, a new method of sterilization has been adopted. There is an electric power plant worked by water turbines, the force being the water which is afterwards sterilized. The two dynamos are run separately, so that there can be no stoppage while one of them is being cleaned or repaired. The force produced is 110 volts, 500 periods per second, which is transformed into an alternating current with a potential power of 17,000 volts. This high-power current is conducted to a so-called ozone battery. Each of the five batteries composing a system consists of three vertical copper plates 2 feet square and  $1\frac{1}{2}$  inches thick, with a space of 8 inches between each; in each of these spaces there is a pair of glass sheets, between which the electric sparks decompose the air, which is forced through them by a sucking machine. The decomposed air consists of ozone and azotic acid. The azotic acid is retained and the pure ozone made available by passing the decomposed air through a vertical vitrified pipe containing charcoal dust and pieces of cement. The water, under the pressure of a fall of 12 feet, flows through a system of earthen tubes about 1 inch in diameter and having 33 holes each; these tubes pass through a space filled with ozone, which the water absorbs.

After this first process of sterilization the water flows into a tank in which there is a wire netting supporting about 3 feet of pebbles; these pebbles divide the water so that it falls like a heavy rain to the bottom of the tank and a strong ozone current, coming from the sides of the tank, is absorbed by the falling water. The ozone is then extracted by having the water fall on stone steps. Medical authorities declare that after having undergone this process water is absolutely germ-free and that it is impossible to produce any kind of germ culture in it.

Two ozone plants were built in 1909: one of them gives an output of 39.61 gallons per second, and the other 79.22 gallons. Each of these plants is composed of two separate systems, so that there can be no possibility of a shortage of water. A new plant is under construction which is to be large enough to supply all the towns and cities between Nice and Mentone, a distance of 24 miles. New water-works are also to be constructed in the near future at both Cannes and Grasse.

#### WORLD METAL PRODUCTION.

(From Consul-General Richard Guenther, of Frankfurt.)

From the annual reports of three German joint stock metallurgical companies, with head offices here, the following translation has been made of certain statistics on metal production and consumption:

The world production of copper in 1909: aggregated 844,100 tons (metric ton = 2,204.6 pounds), which exceeds by about 100,000 tons that of the year before. The United States had the largest share, 498,200 tons, an increase of about 16 per cent. over the output in 1908. The world consumption of copper in 1909 reached 782,800 tons, exceeding that of the preceding year by 85,100 tons. The giant share in the consumption fell to the United States, and amounted to 318,900 tons (against 208,800 tons in 1908); Germany consumed 179,100 tons; England, 109,100 tons; France, 73,100 tons.

The world production of lead last year aggregated 1,052,500 tons, divided thus: Europe, 505,800 tons; United States, 339,700 tons; Mexico, 118,000 tons; Australia, 77,200 tons. The United States consumed 365,200 tons of lead; Germany, 213,200 tons; Great Britain, 199,500 tons; France, 110,400 tons; Russia, 38,300 tons.



Of tin, 108,300 tons were produced in 1909, of which 61,500 tons came from the Straits Settlements ports; 35,600 tons from Bolivia; Germany produced (mainly from Bolivian ores) 8,990 tons. The consumption of tin was distributed: United States, 42,800 tons; England, 17,500 tons; Germany, 17,100 tons; France, 8,750 tons; and Belgium, 1,300 tons.

The zinc production in 1909 was 783,200 tons, of which the United States contributed 240,446 tons; Germany, 220,100 tons; and Belgium, 167,100 tons.

In 1909 the world produced 16,100 tons of nickel, the chief contributors being United States, 9,000 tons; Germany 3,100 and England, 2,800 tons.

Of aluminium, 24,200 tons were produced and 30,800 tons consumed throughout the world, while the production of quick-silver amounted to 3,200 tons, of which Great Britain took 1,445 and Germany 723 tons.

### POTATO STARCH IN GERMANY.

(By Vice-Consul General Frederic W. Cauldwell, of Berlin.)

Potatoes are the principal source of the starch manufactured in Germany, and that potato starch, known as "kartoffelmehl," enters extensively into German export trade.

The potatoes are first thoroughly washed and then mashed between heavy rolling cylinders, on the surface of which there are grooves and teeth to tear up the potato cells. The starch is washed out of this ground-up pulp by means of running water. The resulting so-called "starch milk" is first drained through wire or milk screens or through perforated copper plates to remove the cell pulp, after which it is allowed to flow directly into cement settling vats or caves, or it may first be led over small, gently sloping troughs or drains, upon which the purest of the starch then settles.

The starch from the settling vats and from the settling drains is refined by being rinsed in stirring vats, and the impurities and cell substances are skimmed or dipped off. The water is then removed by special centrifugal hydro-extractors and the resulting so-called "green starch" is generally worked up into dextrin and sugar. For producing the starch of commerce it may be further dried in specially constructed drying chambers. The potato pulp, or cell stuff, left over is subjected to a renewal of the refining process, or it may be dried and fed to stock.

(A detailed report on potato-desiccating machinery, by Consul Thomas H. Norton, of Chemnitz, appeared in *Daily Consular and Trade Reports* of February 19, 1910.)

### IMPORTATION OF TUNGSTEN FROM THE PLAUEIN DISTRICT.

According to Consul Carl Bailey Hurst, tungsten powder, heretofore rarely sent from the Plauen district, was shipped to the United States in 1909 to the value of \$34,996. This metal, produced from wolfram ore found in that district, has been used in Germany in a process for hardening steel. It promises to become an important item of export as it is more extensively taken up in the American steel works.

## OFFICIAL REGULATIONS AND RULINGS.

### NOTICE OF JUDGMENT NO. 497, FOOD AND DRUGS ACT.

IN THE CIRCUIT COURT OF THE UNITED STATES  
SOUTHERN DISTRICT OF IOWA  
CENTRAL DIVISION.

SHAWNEE MILLING COMPANY, Complainant,

vs.

MARCELLUS L. TEMPLE, United States District Attorney, and FRANK B. CLARK, United States Marshal, Respondents.

No. 2490.  
Equity.

THE UPDIKE MILLING COMPANY, a corporation, Complainant,

vs.

MARCELLUS L. TEMPLE, as United States District Attorney for the Southern District of Iowa, FRANK B. CLARK as United States Marshal for the Southern District of Iowa, and A. BROWN, full first name unknown, as Food & Drug Inspector of the United States Department of Agriculture, Respondents.

No. 2492.  
Equity.

### SUITS TO RESTRAIN SEIZURES, UNDER SECTION 10 OF THE ACT, OF COMPLAINANTS' FLOUR BLEACHED BY THE ALSOP PROCESS.

On or about December 14, 1909, the Shawnee Milling Co., a corporation, of Topeka, Kans., filed in the United States Circuit Court for the Southern District of Iowa a bill in equity naming as defendants thereto Marcellus L. Temple and Frank B. Clark, United States Attorney and United States Marshal, respectively, for said district, alleging that said defendants were about to proceed without warrant of law and to the detriment of complainants' rights to make seizures of flour bleached by the Alsop process, under Section 10 of the Food and Drugs Act, and further alleging that said act was unconstitutional, and praying that said defendants be enjoined from proceeding under said act and from making seizures of complainants' flour bleached as aforesaid pending the determination of this case.

Subsequent to the filing of the above bill the Updike Milling Co., a corporation, of Nebraska, filed in said court a similar bill against the same defendants and A. Brown, a food and drug inspector of the United States Department of Agriculture, containing substantially the same allegations and prayers. The material allegations of both bills of complaint appear more fully in the opinion of the court hereinafter set out.

To both bills of complaint the defendants filed a demurrer alleging as grounds therefor that complainants' bill failed to any cause which would entitle them to the relief sought in said bills.

On April 26, 27, and 28, 1910, the cases came on for hearing and the questions of law raised by the bills of complaint and the demurrers thereto were fully argued to the court. On May 10, 1910, after full consideration, the court dismissed complainants' bills, delivering the following opinion:

OPINION.

SMITH MCPHERSON, Judge.

Each of these two cases is by a bill in equity, practically the same. One of the complainants, Updike Milling Company, is a corporation under the laws of Nebraska, there engaged in the business of manufacturing wheat into flour both for domestic use, and for shipments into Iowa and other states for sale and consumption. The other complainant, Shawnee Milling Company, is a corporation under the laws of Kansas, there engaged in a like business, sales and shipments.

The defendants are the United States Attorney and Marshal for this District, and the relief sought is to enjoin the respondent officers from having issued, or serving process for seizing complainants' flour in interstate shipments under the National Pure Food statute of June 30, 1906.

The allegations are that complainants' flour is whitened and aged by a process, and that the same is not harmful, but is more nutritious, wholesome and attractive for making bread. It is not alleged in the bill of complaint in terms that the flour is bleached by the Alsop process as covered by certain English and American patents as set forth by the Circuit Court of Appeals for this circuit in the case of Naylor vs. Alsop Process Company (168 Fed. Rep., 911), but all the arguments, both by briefs and orally, were on that state of facts. Counsel for the

United States have appeared for the defendants, thereby in effect making the cases controversies between the United States Government on the one side, and western flour mill owners on the other, who bleach their flour by the agency of nitrogen peroxide under the Alsop Patent process.

A literal reading of the bills of complaint will show that they are fairly subject to the criticism, that the allegations as to the aging, whitening and improving the flour are largely by the use of adjectives and adverbs, instead of reciting just what is done: how the flour is aged; how whitened; how made more nutritious; why not harmful; and why better by the use of some agency not named nor described. But this criticism need not be elaborated. The cases are now for determination on demurrers to the bills of complaint, and sufficient allegations appear to cover the rulings now to be made.

A bill in equity in which the writ of injunction can issue to enjoin the enforcement of a criminal or penal statute is allowable only when:

1. Such statute is unconstitutional or otherwise invalid;
2. In an attempt to enforce such invalid statute, rights of property are invaded and trampled on; or,
3. The often repeated attempts to enforce such invalid statute creates a multiplicity of actions which are of themselves oppressive.

The important and recent case of *Ex parte Young* (209 U. S. 123) illustrates this, in which case it was held that a bill in equity would confer jurisdiction because of the oppressive penalties if an effort should be made to protect the rights of property. In *City of Hutchinson vs. Beckham* (118 Fed. Rep., 399), the Circuit Court of Appeals for this district held that an injunction should issue against the prosecution of cases under an invalid ordinance requiring an illegal license, which would be followed by many criminal prosecutions. In *Dobbins vs. Los Angeles* (195 U. S., 223,241), the holding was clearly and tersely stated:

"It is well settled that where property rights will be destroyed lawful interference by criminal proceedings under a void law or ordinance may be reached and controlled by a decree of a court of equity."

But if property rights are not invaded, then a court of equity ordinarily will not interfere, because the defense as to the invalidity of the statute can be urged in the criminal or penal action or special proceeding. Thus, in the case of *In re Sawyer* (124 U. S., 200) it was held that proceedings for the ouster of a city officer could not be enjoined for the alleged invalidity of the law under which the proceedings were being conducted. And of like holdings are the cases of *Hardrader vs. Wadley* (172 U. S., 148), and *Fitts vs. McGhee* (172 U. S., 516).

And if the proceedings for seizure are to be regarded as civil, then section 723, R. S., will prohibit the filing of a bill in equity to enjoin the enforcement of a valid statute.

In the one case now before the court, the bill of complaint recites that several seizures of flour were made in this judicial district, and after a number of efforts by the complainant to have the cases submitted to the court with or without a jury for a hearing on the merits, the Government dismissed the cases, after the flour thus seized had deteriorated in quality and value.

In the cases now before the court as property rights are involved, bills in equity will be entertained, *provided* the statute under which the Government claims the rights to proceed is not a valid one. Herein is the question in the case; that is to say, Is the pure food statute of June 30, 1906, a valid enactment? Did Congress have the power to enact it? Is it within the commerce clause of the Constitution, or is it a mere police regulation erroneously garbed and cloaked as a regulation of commerce?

Good, sound wheat of the best variety, properly and timely harvested, put through the "sweat" in the stack, well ground and bolted, makes nutritious, wholesome, and white flour.

This fact is so generally known that courts will take judicial notice of the fact.

It is said that flour made from new and poorer wheat, not "sweated," and made by the process covered by the English patent of Andrews, or the American patent of Alsop as illustrated in the patent decision hereinbefore referred to (168 Fed. Rep., 911), will also be equally white. This is quite likely true. But is it equally pure, equally nutritious, or is it adulterated and poisoned?

This court in these cases is not to decide those questions. Nitrogen peroxide under the Andrews patent is produced by combining nitric acid with a metallic compound. Under the Alsop patent it is produced by subjecting atmospheric air to a flaming electric arc. It is claimed by some that nitrogen peroxide is the agent for bleaching flour under both patents, while others claim that it is the ozone that does the effective work, while the nitrogen peroxide is a by-product when the ozone is thereby created.

Whatever the truth is as to what does the bleaching, it is both claimed, and denied, by chemists who ought to be able to agree, that the flour is poisoned by such process. But it is known that after the air is thus subjected to continuous flaming electrical discharges, that the result and gas is conveyed by means of pipes to a compartment and there is commingled with the flour agitated or in a cloud, and thus subjected to said treatment it becomes dry and white. The result of it all is that new wheat and of an inferior quality is converted into flour with the appearance of flour from a better wheat that has been aged by time.

The Government contends that flour thus bleached is flour in the language of the statute "whereby inferiority is concealed," and that "it contains added poisonous ingredient which may render such article (flour) injurious to health." The patentees and the millers deny this.

Here is a question for determination by a jury, or by the court if a jury is waived, and not to be determined in this case if the statute is valid.

Several of the states within the past few years have enacted pure food statutes. Congress June 30, 1906, enacted the statute in question. All these statutes were enacted to cure evils well nigh intolerable that had grown up during this age of greed and avarice and commercialism that has made money-getting the prime object of life with so many. The evils were such that much of the foods we ate, whether meats of any kind, including fish, and poultry, or fruits in all forms, and breadstuffs, were so adulterated and "loaded" or "doctored" as to deceive the consumer. And the same was true of flavors and condiments. The evil as to confectionery and flavors and extracts was as great. Still greater was the evil as to drugs and medicines. In fact the evils were everywhere present, as to food and medicine, and other things. And to eliminate some of these evils and to enable the purchasers to receive what they ordered and paid for, many states passed statutes aimed at those frauds. But it was soon found that the states in some instances were disposed to condone as to some articles of local manufacture, and in many other instances the states were powerless to work out a remedy. Thereupon Congress, acting upon the theory that the evil was of national concern, enacted the statute in question. The debates in Congress show that the measure was earnestly fought as being one of paternalism, and a police regulation with which the states only could act.

The Secretary of Agriculture, Mr. Wilson, performed his duty both in letter and spirit when he submitted the question as to flour bleached by nitrogen peroxide to the Board of Food and Drug Inspection. And the board, the Secretary concurring, after a hearing given to all parties in interest, found that such flour is in contravention of the statute. Such finding is not binding as against the parties thus bleaching flour. But it is

conclusive as against all criticism for making the seizures and bring the question before the courts for determination.

Congress is given the power to provide for the general welfare of the United States. But without doubt if this legislation is sustained, it is because of that provision of the Constitution that provides that Congress shall have the power to regulate commerce among the several states. That provision is the life of the nation, and to adopt which was the great concern of the convention of 1787. Important as it is, it is ever before the courts. It gives great comfort to all who believe in one common country, and yet is antagonized oftener than any other provision of the Constitution, by those whose shield of defense is articles 9 and 10 of the amendments, as to the reserved power of the States.

No one claims that Congress can be the sole judge of its powers. All thoughtful persons concede that any court having jurisdiction in the first instance must pass upon the question of the powers of Congress, and that it is for the Supreme Court in the end to finally set the matters at rest. But so careful have our Congresses and Presidents been, that for the first hundred years of our Government, the Supreme Court found it necessary to hold that Congress had exceeded its powers in only twenty instances. (See Appendix to Volume 131, U. S. Reports, p. cxxxv.) And of those twenty statutes thus held void, not one related to commerce. Since then, the Supreme Court has held three Congressional enactments void. One was a statute making a judgment of convicting conclusive evidence against a party in another case. (*Kirby vs. U. S. Farmers Loan Co.*, 157 U. S., 429, and 158 U. S., 601.) The other, and only one from the organization of our Government to date as to commerce, is that of the employers' liability statute, enacted under the claim that the commerce clause would sustain it. (The Employers' Liability Cases, 207 U. S., 463.) If other enactments of Congress have been held void by the Supreme Court such cases have been overlooked, and it is believed there are none other. There are almost innumerable decisions touching the power of the states with reference to commerce. It would be to no purpose to discuss many of these authorities. And it would be needless waste of energy to discuss the many decisions relating to the use of the mails, for the obvious reason that a distinct clause of the Constitution empowers Congress to control our postal system, and there is not the slightest difference whether the mails thus carried are state or interstate.

Neither the court nor the parties are aided by a review of those matters. It must be and is conceded that police regulations alone are for the State, and not for Congress to deal with.

But it does not follow that if the subject matter to be regulated is one of commerce, that it is for the state alone to deal with, because such subject matter is also one that pertains to the morals, health, or good order of the community.

Thus when the question arose as to the inspection of meats for food, legislatures claiming that they alone could determine when and to what extent police regulations should be carried, the Supreme Court decided that such inspection also impinged upon the rights of commerce and were therefore void. (*Minnesota vs. Barber*, 136 U. S., 313; *Brimmer vs. Rebman*, 138 U. S., 78.)

It will serve no purpose to discuss the principle upheld in *Wilson vs. Blackbird Creek Company* (2 Peters, 245), that the State can regulate certain interstate commerce of a local character, if Congress had not acted, nor of that other principle upheld by Congress that the State can legislate with reference to liability of a party when doing an interstate business when Congress has not acted. (*Sherlock vs. Alling*, 93 U. S., 99.) The complete answer to those suggestions is that in the matter now before the court, Congress has acted. The question now for consideration is not as to the power of the State relating to commerce, as held in *Smith vs. Alabama* (124 U. S., 463), up-

holding a state statute requiring a locomotive engineer even though operating an interstate train to submit to tests for color blindness.

The question here is as to the power of Congress over articles of interstate commerce, even though such articles in the end become subject to state statutes. No one doubts but that wheat and flour, as well as all articles of food, are subjects of commerce, and when carried over and across state lines, are subject to be regulated by Congress. And it is no answer to say, that when adulterated, or wrongly labeled, because in the end they will fall under a state statute, that they when being shipped can not be covered by a congressional enactment. The liquor cases illustrate this. Because of all the subjects of commerce there is no one thing more peculiarly and distinctly and appropriately subject to regulation by the State even to the extent of prohibition than are intoxicating liquors. And yet Congress legislates with reference to liquors. The Wilson Act of 1890 provided that when liquors arrived in a State they should be subject to State laws. This statute was upheld in the case in *re Rahrer* (140 U. S., 545), thereby modifying the practical effect of the holding in *Leisy vs. Hardin* (135 U. S., 100), that the State could not interfere by legislation as to liquors shipped interstate as long as the liquors were in the original packages, while in *Rhodes vs. Iowa* (170 U. S., 412), it was held that the liquors must be in fact and actually delivered to the purchaser before the State laws became effective as to such interstate shipment. No one should doubt but that legislation by Congress can control the interstate subject of commerce for a time at least, and then the State by a police regulation can control.

If liquors do not sufficiently illustrate the question, lottery tickets will. The Louisiana Lottery was conducted by men of high repute and much renown. But it became a national scandal. It was struck at by denying it the use of the mails. The legislature of the State gave it encouragement; even its life. But Congress provided in addition that it should be a crime to carry lottery tickets from one State to another by means other than through the mails. Can any person doubt but that the Louisiana Lottery was or could have been made subject to the laws of Louisiana? And yet this congressional enactment was upheld in the Lottery Case (188 U. S., 321). But little need be said of that case. It was argued by counsel of great eminence. It was argued upon two separate occasions. It received the fullest consideration by the Supreme Court. Apparently no other case that was ever before that court received more attention and fuller consideration. Counsel for complainants herein concede all these things. And the only answer that has been made, or that can be made to that case, is in the statement that the case was decided by a divided court, four justices dissenting. It may be, or it may not be, that that weakens the case as an authority. It is barely possible that later on, that court changing as to its personnel, the decision may be overruled. But such reasoning is a mere speculation. On the other hand the fact that the court was so divided emphasizes the fact that the court gave great consideration to the question. But be these things as they may, it is not for this court to usurp the prerogative by blindly declining to follow that decision. That decision stands, and as long as it stands, it is the law of the country, and this court not only must, but does cheerfully observe it in all its phases.

Much more could be said. Cases commencing with *Gibbons vs. Ogden*, and then to date, could be reviewed. The question could be illustrated in many ways. But all that would be to no purpose; it would be academic.

Congress has enacted a safety appliance law for the preservation of life and limb.

Congress has enacted the anti-trust statute to prevent immorality in contracts and business affairs.



Congress has enacted the live stock sanitation act to prevent cruelty to animals.

Congress has enacted the cattle contagious disease act to more effectively suppress and prevent the spread of contagious and infectious diseases of live stock.

Congress has enacted a statute to enable the Secretary of Agriculture to establish and maintain quarantine districts.

Congress has enacted the meat inspection act.

Congress has enacted the employers' liability act.

Congress has enacted the obscene literature act.

Congress has enacted the lottery statute above referred to.

Congress has enacted (but a year ago) statutes prohibiting the sending of liquors by interstate shipment with the privilege of the vendor to have the liquors delivered c. o. d., and to prohibit shipments of liquors except when the name and address of the consignee and the quantity and kind of liquor is plainly labeled on the package.

The statutes, police regulations in many respects, are alike in principle to the act of June 30, 1906, under consideration. Can it be possible they are all void?

This statute by its title, and by its every provision plainly shows that it is with reference to commerce, and that it is not with reference to local police regulations.

It is also contended that so much of Section 7 of the statute as relates to food is void because no standard has been fixed.

That argument is made because drugs are fixed by a standard recognized by the United States Pharmacopoeia or National Formulary, and as to confectionery a standard is fixed by declaring what confectionery *shall not* contain. Whereas as to foods no standard has been fixed. It is a fact most obvious that no standard could be fixed other than was done by Congress. The one provision as to food is, that it shall not be mixed so as to reduce or lower or injuriously affect its quality or strength. Another provision is that some substance shall not be substituted wholly or in part for the article. Another provision is that no valuable constituent of the article shall be abstracted. Another provision is that it shall not be mixed, colored, powdered, coated, or stained in a manner whereby damage or inferiority is concealed. Another provision is that poisonous or other deleterious ingredients shall not be added. Still another provision is that filthy, decomposed, or putrid substance shall not be added. And so on more in detail than herein enumerated. These provisions present questions of fact as to every alleged contraband article. This objection is without merit.

This case was argued upon both sides with most signal ability, displaying much learning, and was argued at great length. The case has received from this court the fullest consideration, and the conclusions are that these bills in equity cannot be maintained, and therefore will be dismissed.

DES MOINES, IOWA, MAY 10, 1910

JAMES WILSON,  
Secretary of Agriculture.

WASHINGTON, D. C., June 25, 1910.

#### NOTICE OF JUDGMENT NO. 498, FOOD AND DRUGS ACT.

In the case of the United States ex rel. Alsop Process Company, petitioner, vs. James Wilson, Secretary of Agriculture, a mandamus proceeding in the Supreme Court of the District of Columbia to restrain the Secretary of Agriculture from publishing and circulating Food Inspection Decision No. 100 of the United States Department of Agriculture relative to flour bleached by the Alsop Process, and to compel cancellation of said decision.

On or about January 23, 1909, the Alsop Process Company filed in the Supreme Court of the District of Columbia a petition for a writ of mandamus directed to the Secretary of Agriculture alleging in substance that relator is a corporation engaged in the

business of manufacturing and selling machinery and apparatus used by millers for the bleaching of flour by so-called Alsop Process (giving a description of said process), and further, that the Secretary of Agriculture caused hearings to be held to determine whether flour bleached by the Alsop Process was adulterated within the provisions of the Food and Drugs Act of June 30, 1906, and after hearing the evidence for and against flour thus bleached, decided that, in his judgment, flour so bleached was adulterated within the meaning of the aforesaid act, and that the Secretary of Agriculture, without warrant or color of law, published and caused to be published the said decision designated as Food Inspection Decision No. 100, which publicly condemned as adulterated within the meaning of the Food and Drugs Act flour bleached by relator's process to the great damage of its business. The petition prayed that the Secretary of Agriculture be commanded to revoke and cancel and annul said decision and not to deliver or circulate additional copies thereof.

Upon the filing of the petition the court issued a rule directed to the Secretary of Agriculture as respondent requiring him to show cause by a certain date therein named why the prayer of said petition should not be granted.

Respondent duly answered said petition and to this answer the relator filed a demurrer. The case came on for hearing upon the questions raised by the above-mentioned pleadings and the court overruled relator's demurrer. The following is the opinion of the court delivered by Mr. Justice Stafford:

IN THE SUPREME COURT OF THE DISTRICT OF COLUMBIA.

UNITED STATES OF AMERICA EX REL. ALSOP PROCESS	} At Law No. 51348
COMPANY, Petitioner,	
JAMES WILSON, SECRETARY OF AGRICULTURE,	
Respondent.	

#### OPINION OF THE COURT.

By STAFFORD, J.

This is a petition for a writ of mandamus. A rule to show cause was issued which the respondent has answered and to this answer the petitioner has demurred. The case was heard upon the demurrer and would have been disposed of at the time had it not been that the court understood that the parties desired that an opinion should be filed dealing fully with all the points involved. The case has been left undisposed of in the hope that opportunity would be found to prepare such an opinion, but the pressure of other duties having thus far prevented, and no likelihood appearing that the same can be done within the next few days, it is thought best to dispose of the case without answering categorically the numerous points made in the brief of the petitioner. After all what the case amounts to is this. The Secretary of Agriculture has made up his mind that bleached flour is obnoxious to the provisions of the pure food act and has made that opinion public, announcing at the time that after six months, during which time the manufacturers and dealers will have an opportunity to adjust themselves to the situation, he will call upon the respective district attorneys to proceed against violators of the law. The petitioner claims to be the owner of a patent on the bleaching process and to be injured by the announcement of this opinion and intention. He is not the owner of any flour; he merely owns the patent and makes and sells the machinery. He says that the Secretary did not proceed according to the provisions of the pure food law in making up his mind; that he had no right to tell the public what opinion he had formed, nor what course he intended to pursue; that if he is going to recommend prosecutions at all he is bound to do so at once and not wait six months. He therefore asks this court, by the great writ of mandamus, to command the Secretary to vacate his decision, to take back what he has said, and hereafter to proceed strictly according to the law. The mere statement of the proposition seems to furnish its own

answer and to render an elaborate opinion unnecessary. This court cannot change the fact that the Secretary entertains this opinion, nor the fact that he intends to call on the district attorneys to test the case in the courts. It cannot command him not to make his opinion and intention known and if it could it would be useless for he has already made it known, and the petitioner itself is making the fact still more widely known by this proceeding. The merits of the real question, namely, whether flour subjected to the bleaching process may be sold without violating the pure food law, is one that will ultimately be determined by the courts. In the meantime the Secretary is not violating any law in having an opinion and in telling the public what it is.

The demurrer is overruled.

WENDELL P. STAFFORD,  
*Justice.*

The said Alsop Process Company stood upon its demurrer and prosecuted an appeal from the aforesaid judgment to the Court of Appeals for the District of Columbia. The case was then heard by said court on appeal and the judgment of the lower court was affirmed. The following opinion by Mr. Justice Robb was rendered by the appellate court:

UNITED STATES OF AMERICA EX RELATION ALSOP PROCESS COMPANY, <i>Appellant</i> ,	} No. 2021.
VS.	
JAMES WILSON, SECRETARY OF AGRICULTURE.	}

This is an appeal from the Supreme Court of the District overruling the demurrer of the relator to an answer of the defendant, appellee, here to a rule to show cause why a mandamus should not be issued against him.

In its petition the relator states that it is a corporation of the State of Missouri engaged in the manufacture of flour bleaching machinery, which is sold throughout the United States and elsewhere and is extensively used by millers for bleaching flour. The process for which this machinery is designated is known as the "Alsop Process" and is covered by patent which is owned by the relator. The bleaching of flour by this process is accomplished by the passage of pure air through a flaming discharge of electricity and the application of the resultant gaseous medium to the freshly milled flour as the latter passes through an agitator. The flour thus treated, the relator states, has no substance mixed and packed with it so as to reduce or lower or injuriously affect its quality or strength, is not deprived of any valuable substance, nor has it been mixed, colored, or treated in any manner whereby inferiority is concealed, and contains no deleterious ingredient or other element injurious to health. The relator further states that prior to November 18, 1908, the Secretary of Agriculture inserted, or caused to be inserted, in certain milling journals and other periodicals throughout the country a notice to the effect that a hearing would be held on the subject of bleached flour at the Department of Agriculture on November 18, 1908, at which time the relator says it was present by a duly authorized officer and by an attorney, and that the hearing was also attended by many millers from various parts of the country; that this hearing was continued five days, and testimony for and against said process was introduced; that the attorney for the relator conducted the case for the millers favoring the bleaching process; that the relator's manager gave extended testimony at this hearing; that the entire proceedings were transcribed by a stenographer and made accessible to the public generally. This hearing, the relator avers, was without color of authority of law. The petition further states that on the 10th of December, 1908, the said Secretary of Agriculture unlawfully, arbitrarily, and oppressively, and without color or right of law issued, the following bulletin:

#### FOOD INSPECTION DECISION 100.

##### *Bleached Flour.*

"Flour bleached with nitrogen peroxide, as affected by the Food and Drugs Act of June 30, 1906, has been made the subject of a careful investigation extending over several months.

"A public hearing on this subject was held by the Secretary of Agriculture and the Board of Food and Drug Inspection, beginning November 18, 1908, and continuing five days. At this hearing those who favored the bleaching process and those who opposed it were given equal opportunities to be heard.

"It is my opinion, based upon all the testimony given at the hearing, upon the reports of those who have investigated the subject, upon the literature, and upon the unanimous opinion of the Board of Food and Drug Inspection, that flour bleached by nitrogen peroxide is an adulterated product under the Food and Drugs Act of June 30, 1906; that the character of the adulteration is such that no statement upon the label will bring bleached flour within the law; and that such flour cannot legally be made or sold in the District of Columbia or in the Territories; or be transported or sold in interstate commerce; or be transported or sold in foreign commerce except under that portion of Section 2 of the law which reads:

"\* \* \* Provided that no article shall be deemed misbranded or adulterated within the provisions of this act when intended for export to any foreign country and prepared or packed according to the specifications or directions of the foreign purchaser when no substance is used in the preparation or packing thereof in conflict with the laws of the foreign country to which said article is intended to be shipped; \* \* \*

"In view of the extent of the bleaching process and of the immense quantity of bleached flour now on hand or in process of manufacture, no prosecutions will be recommended by this Department for manufacture and sale thereof in the District of Columbia or the Territories or for transportation or sale in interstate or foreign commerce, for a period of six months from the date hereof.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., December 9, 1908."

The promulgation and circulation of this bulletin, the relator states, has worked irreparable harm and injury to it, and in effect deprived it of its property without due process of law "in that since the issuance and promulgation of said unlawful decision aforesaid by the respondent herein, and by reason thereof your petitioner has been unable to sell its patented process and apparatus aforesaid, the prospective purchasers of said patented process and apparatus aforesaid, refusing to buy and install the same for fear that they or their customers will, upon the recommendation of the Secretary of Agriculture, be prosecuted for manufacturing or selling an adulterated food product in violation of the provisions of said Food and Drugs Act, June 30, 1906." The petition closes with a prayer that the writ of mandamus issue to compel the Secretary of Agriculture to withhold recommendation of prosecutions against manufacturers of and dealers in flour bleached by said Alsop Process; to revoke, cancel and annul said decision of said Secretary, and not to deliver or circulate additional copies thereof, and that the Secretary of Agriculture be commanded to proceed relative to the subject of bleached flour in strict conformity with said Food and Drugs Act and the regulations of the Department promulgated thereunder.

A rule to show cause was issued. In the answer filed by the Secretary he states "that it does not appear by the said petition that the said relator has any right, title, or interest in the matters affected by the judgment and action of your respondent referred to in the said petition, and is not a party to nor legally interested in the proceedings in which said judgment and action of your

respondent have been made." He admits the relator owns the patent known as the "Alsop Process" for bleaching flour, but claims that its patented rights are wholly collateral to the right of said Secretary of Agriculture to decide whether flour bleached by the use of nitrogen peroxide is deleterious and adulterated within the meaning of said Food and Drugs Act; that the patenting of said process confers no right on relator and gives it no status to compel the respondent to change or revoke his decision that flour so bleached is adulterated. The answer denies that the effect of flour by the use of said process is as stated in the petition; on the contrary, the answer states "that the flour which is bleached is reduced and lowered in its quality and strength; that the said flour is so artificially colored as to conceal inferiority, and that it contains a poisonous and deleterious ingredient which has been added, and that the said flour is deleterious and injurious to health." The respondent in his answer further says "that the bleaching of the said flour is affected by nitrogen peroxide, and that the resultant product is deleterious and is adulterated within the meaning of the aforesaid Food and Drugs Act approved June 30, 1906"; that for many months prior to November 18, 1908, the respondent had made an exhaustive inquiry into the character, composition and purity of bleached flour and had caused the matter to be investigated exhaustively by the Bureau of Chemistry of his Department, and "that from all the evidence adduced it was conclusively established that flour bleached with nitrogen peroxide was adulterated within the meaning of said Food and Drugs Act;" that in the exercise of abundant caution, however, the Secretary decided to renew the investigation and to consider the matter more fully before finally deciding under the authority of said Act whether said bleached flour was adulterated; that accordingly he issued a notice for said public hearing; that this hearing was entirely advisory; and that the millers and manufacturers and others who attended did so voluntarily. The result of this hearing, the Secretary says, was to put him in possession of further and additional evidence relative to the subject; that this hearing was authorized both impliedly by the provisions in said Food and Drugs Act and expressly by the provisions of the Agricultural Appropriation Act of Congress of May 23, 1908; that after due consideration he decided that flour bleached by the use of nitrogen peroxide is adulterated within the meaning of said Food and Drugs Act and forbidden by the terms of said Act, and that he thereupon announced and published said decision of December 10, 1908; that this decision in no wise mentioned or in any way relates to the relator, and that, therefore, it has no status to seek any relief or redress in connection therewith. The Secretary in his answer denies the averments of the petition that his action was without right or color of law, denies the jurisdiction of the court to grant the writ, and states that he "passed no judgment upon the machinery of the relator, and has no jurisdiction over the same, nor concern therewith. The said relator is not an owner of bleached flour nor a manufacturer of the same. The judgment of the said respondent has to do only with the bleached flour, the product itself, and has no jurisdiction over or concern in one of the kinds of process by which the said product may be secured. And respondent submits that the claims of the said relator are wholly collateral, and that its petition fails to show any legal damage."

To this answer a demurrer was filed, which was overruled, and, relator choosing to stand upon its demurrer, final judgment was entered, and this appeal taken.

The first question to be disposed of is whether the interest of the relator in the subject matter involved is of such a nature as to entitle it to maintain this proceeding. The decision of

the Secretary of Agriculture, which is here sought to be challenged, is to the effect that flour bleached by nitrogen peroxide is an adulterated product under said Food and Drugs Act. Neither the relator nor its process is mentioned in this decision. The relator is neither the owner nor the manufacturer of bleached flour. Its sole excuse for attempting to stay the hand of the Secretary is that since the promulgation of this decision by the Secretary it has been unable to sell its patented process and apparatus owing to the fear of prospective purchasers that upon the recommendation of the Secretary they will be prosecuted for manufacturing or selling an adulterated food product.

While it is true that there is a distinction between cases where the extraordinary aid of mandamus is invoked merely for the purpose of enforcing or protecting a private right and cases where the purpose of the application is the enforcement of a purely public right, the people at large being the real party in interest (High on Extraordinary Remedies, *Par. 430; 26 Cyc 404* and cases there cited), it has never been held, at least to our knowledge, that such an indirect and collateral interest as is here shown will sustain a petition for the writ.

The relator as a corporate entity has no interest in the enforcement of duties owing by the Secretary to the public. It seeks to arrest the operations of an Executive Department of the Government solely because the indirect effect of the promulgation of an opinion by the head of the Department has been to cause millers to cease purchasing relator's machinery. In all the cases relied upon by relator mandamus was granted to secure to the relator's rights which they were entitled personally to enjoy. Measured by this test, it is apparent that the relator has no such interest in the subject matter of this controversy as to entitle it to the writ. Being neither an owner nor a manufacturer of bleached flour, its legal rights were not involved or invaded by the action of the Secretary. It is a mere volunteer in this proceeding and as such is without standing.

There is some analogy between a suit in equity for the abatement of a public nuisance and the present case. Yet it is well settled that such a suit will not be sustained unless the complainant shows special, direct, and material damages; *Georgetown v. Alexandria Canal Co.*, 12 Peters, 91; *Irwin v. Dixon et al.*, 9 How. 9; *State of Penna. v. Wheeling Bridge Co., et al.*, 13 How. 518; *Miss. & Mo. R. R. Co. v. Ward*, 2 Black, 485. In the case last cited it was said: "A bill in equity to abate a public nuisance, filed by one who has sustained special damages, has succeeded to the former mode in England of an information in chancery, prosecuted on behalf of the Crown, to abate or enjoin the nuisance as a preventive remedy. The private party sues rather as a public prosecutor than on his own account; and unless he shows that he has sustained, and is still sustaining, individual damages, he cannot be heard."

The rule permitting private parties, whose rights are directly jeopardized, to maintain mandamus to compel a public duty is a salutary one, but it should not be enlarged to such an extent as to permit interference with the operations of the Government by those whose rights are only remotely and indirectly affected.

Having determined that the relator's interest in the subject matter involved is too remote to entitle it to institute this proceeding, it becomes unnecessary to consider any other question.

The order is, therefore, affirmed, with costs.

CHAS. H. ROBB,  
*Associate Justice.*

AFFIRMED.

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., June 25, 1910.



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### ALBERT ERNEST LEACH.

April 7, 1864.

August 22, 1910.

Instances are not uncommon of men who have become famous in youth and died in early manhood, or who did not find their calling until late in life and achieved fame in old age, but it is rare indeed that men begin their life work well along in manhood and end a distinguished career in middle life.

Albert Ernest Leach belongs in the last-named class. Although he did not join the chemical fraternity until after he had become an expert in another calling, he soon won for himself a foremost place among food chemists and in less than fifteen years accomplished work that well might have been distributed through a long life.

Mr. Leach was born in Boston, April 7, 1864, and died in Denver, August 22, 1910.

He was graduated from the Newton (Mass.) High School in 1882, and from the Massachusetts Institute of Technology, with the degree of S.B., in 1886, after completing the course in mechanical engineering. Although specializing in mathematical and mechanical studies, he devoted considerable time to chemistry, thus laying the foundation for his subsequent career.

In 1887 he entered a patent law office, where after five years' service he acquired the reputation of an expert in mechanical electrical and chemical cases. Although these years in the law office were lost so far as laboratory experience was concerned, they were of inestimable value in developing the remarkable ingenuity afterwards displayed in devising analytical methods, and in acquiring the art of clearness and exactness of expression, of which he became a master.

In 1892 he gave up patent law and entered the laboratory of the Massachusetts State Board of Health as assistant analyst. Feeling the need of further chemical training, he found time during the years 1894, 1895 and 1896, without giving up his position with the Board of Health, to complete two years of postgraduate study at his Alma Mater, the subjects covered being industrial, theoretical and sanitary chemistry and quantitative analysis. This work was not done with a view of attaining an advanced degree, as he took no examination whatever during his graduate study.

His position with the Massachusetts State Board of Health was exceptionally fortunate. Not only was this institution the pioneer in the country in food inspection, but it numbered among its officers such men as Dr. Abbott, Secretary of the Board, Dr. Brown, the well-known sanitary chemist, and Dr. Worcester, analyst in charge of the Food and Drug Laboratory, all men of high attainment and noble ideals, who had brought the Board up to a high degree of efficiency. For these men Mr. Leach acquired not only respect but affection, as evidenced by the dedication of his "Food Inspection and Analysis" to Dr. Worcester and the acknowledgments in the preface.

After the untimely death of Dr. Worcester from the very disease that later claimed Mr. Leach as a victim, the Board hesitated in its selection as a successor. Since up to that time the position of analyst had been filled by a doctor of medicine, he who was destined to fill soon a unique position among food chemists was all but rejected in the vain search for a medical man with training quite foreign to his profession. Mr. Leach was, however, appointed in 1899.

The amount of work accomplished by Mr. Leach during the few years he served as analyst of the Massachusetts State Board of Health is indeed extraordinary. In addition to the official inspection, involving the examination of some ten thousand samples annually, and frequent appearance in court,

he found time for devising important analytical processes, the publication of papers on the composition and analysis of foods in scientific journals and official reports, the instruction of pupils in the analysis and microscopy of food and drugs, the delivery of courses of lectures on food inspection and analysis at the Massachusetts Institute of Technology and the Brooklyn Polytechnic Institute, as well as popular talks before various clubs and organizations, the study of methods as a referee of the Association of Official Agricultural Chemists, and finally the Herculean task of writing a comprehensive work of over eight hundred pages—"Food Inspection and Analysis."

He joined the Bureau of Chemistry, U. S. Department of Agriculture, in 1907, as Chief of the Denver Food and Drug Laboratory, although his health was such that for some time he was not able to enter fully on the duties of the office.

At the time the American Chemical Society organized This Journal, Mr. Leach was chosen a member of the Board of Editors. He served on the board until his death, reading all papers connected with food chemistry and analysis.

At the time when his recovery seemed an accomplished fact, he was stricken by a new form of the disease that previously had laid him low, and died after a wasting illness of some months, retaining his mental powers until the very end.

He is survived by his wife, neé Martha Hughes Thompson, to whom he was married on Sept 2, 1890, three daughters and one son, the latter a Sophomore in the University of Colorado, specializing in chemistry.

Mr. Leach's methods of analysis were at once ingenious and timely. His refractometric method of detecting wood alcohol in liquor was devised at the time when this adulterant was causing havoc among the consumers of cheap liquors and at once superseded the laborious and unsatisfactory methods then in vogue. He also applied the different forms of refractometer to various other new lines of investigation not thought of by the originators of the apparatus, thus greatly enhancing the value of the instrument in the food laboratory.

His procedure in milk analysis was not only rapid, permitting the inspection of large numbers of samples daily, but complete in details for the detection of watering, skimming, preserving and coloring of the product. The fraud of coloring blue milk yellow might long have escaped detection had it not been for his analytical scheme. He was a pioneer in the examination of condensed milk and the methods proposed by him are to-day widely used for purposes of inspection. His work on vinegar was also path-breaking and of special value in diagnosing skilfully concocted imitations of cider vinegar.

Among the other products which he specially studied were molasses, glucose, corn oil and various other oils and fats, mustard and other spices and drugs.

As a man, Mr. Leach was at once strong and gentle; honorable in all his dealings with members of the profession and the outside world, sympathetic with all in trouble, a true friend and conscientious adviser. A follower of Swedenborg, his work and life were a part of his religion.

Following is a partial list of his publications:

"Character and Extent of Food Adulteration in Massachusetts." Read before the Society of Arts, Boston, and published in the *Technology Quarterly*, Vol. 13, p. 22.

"Foreign Coloring Matter in Milk." *Jour. Am. Chem. Soc.* Vol. 22, p. 207.

"Estimation of Fat in Condensed Milk." *Loc. cit.*, supra, p. 589.

"Microscopical Examination of Foods for Adulteration." Illustrated with 15 plates of photomicrographs. An. Rep. Mass. Board of Health, 1900, p. 679.

"Report on Arsenic and Other Poisons in Manufactured Goods." *Loc. cit.*, supra, p. 695.

"Systematic Inspection of Milk for Preservatives." *The Analyst* (London), Vol. 26, p. 289.

"Foods: Methods of Inspection and Analysis." Signed article in *Reference Handbook of the Medical Sciences*, Vol. 3, p. 180, et seq.

"Provisional Methods for the Analysis of Saccharine Products of the Assn. of Official Agrl. Chemists." U. S. Dept. of Agric., Bur. of Chem., *Bull.* 65, p. 43.

"The Determination of Commercial Glucose in Molasses, Syrups and Honey." *Jour. Am. Chem. Soc.*, Vol. 25, p. 982.

"The Determination of Commercial Glucose in Some Saccharine Products." Proc. of 20th An. Convention of the A. O. A. C., U. S. Dept. of Agric., Bur. of Chem., *Bull.* 81, p. 73.

"Reports as Associate Referee on Dairy Products of the A. O. A. C." *Loc. cit.*, supra, p. 25. Also Bur. of Chem., *Bull.* 90, p. 75, and *Bull.* 99, p. 78.

"Composition and Adulteration of Ground Mustard." *Jour. Am. Chem. Soc.*, Vol. 26, p. 1203.

"The Composition of Turmeric." *Loc. cit.*, supra, p. 1210.

"Cider Vinegar and Suggested Standards for Purity." (With H. C. Lythgoe, assistant analyst.) *Loc. cit.*, supra, p. 375.

"A Comparative Refractometer Scale for Use with Oils and Fats." (With H. C. Lythgoe.) *Loc. cit.*, supra, p. 1193.

"The Detection of Watered Milk." (With H. C. Lythgoe.) *Loc. cit.*, supra, p. 1195.

"Some Phases of Food Adulteration and Inspection." Read before the Dept. of Health of the Am. Social Science Assn. of Boston, 1904. Published in *Jour. Am. Soc. Sci. Assn.*, No. 42, p. 110.

"Food Inspection and State Control." Read before the Vermont School of Health Officers at Burlington, 1904. Pub. in the Sept. *Bull. Vt. State Board of Health*.

"The Adulteration of Drugs." Address before the International Pure Food Congress at St. Louis, 1904. Pub. in the Proc. of the 8th An. Convention of State Dairy and Food Depts.

"The Detection and Determination of Ethyl and Methyl Alcohols in Mixtures by the Immersion Refractometer." (With H. C. Lythgoe.) *Jour. Am. Chem. Soc.*, Vol. 27, p. 964.

Reports of the Analyst of the Mass. State Board of Health, 1899-1906, inclusive.

"Food Inspection and Analysis." Published by John Wiley & Sons, New York and London, 1st edition, 1904, pp. 786. 2d edition, 1909, pp. 954.

A. L. WINTON.

## EDITORIALS.

## CAST COPPER.

THOSE who were fortunate enough to attend the Chicago Meeting of the American Electrochemical Society had the privilege of inspecting samples of copper castings made by the process worked out by Dr. Weintraub in the Research Laboratory of the General Electric Company at West Lynn, Mass. Dr. Weintraub's paper (which was read by Mr. Marvin, of Chicago, Dr. Weintraub not being present at the meeting) appears in this number. The castings exhibited at the meeting appeared to be as perfect as the most critical could desire, homogeneous, dense and free from flaws—of very different appearance from castings made in the old ways. Dr. Weintraub obtains his results by the use of boron, the preparation of which in the pure state has also been worked out by himself during recent years. Copper is one of the most beautiful of metals, and in the form of castings made by this process its attractiveness appears to be enhanced visually, as well as by the knowledge of its peculiar physical properties, including a greatly increased conductivity. The new uses to which copper cast by this process can be put are probably very great. But immediately its greatest field of usefulness will be in applying uniform cast metal where formerly joints, brazed and otherwise, were the rule. In this field alone the use of copper will naturally increase and also naturally it will be more valuable insofar as it is better adapted to a particular purpose. This invention will probably prove one of the greatest contributions to the arts in recent times.

## PHOTOGRAPHY.

THE increase in the use of photography and the improvements in the practice are astonishing. Without dwelling upon the development of the portable camera, adapted to a great variety of uses including ultra-rapid photography and for which no better name has been devised than the "hand camera," it is only necessary to observe that no modern family is complete without one of the numerous forms. Neither do we care to consider at length the domain lying between ordinary photography and art—art photography, if you please—where the tendency is toward softness of outline, contrasted effects, separation into planes and wherein the lenses are purposely left more or less uncorrected to produce such effects. What the technical man and chemist want is photographic detail and usually they can not get too much of it. A long series of papers might be written on the modern technical and scientific uses of photography, which would lead from simple detail photography of apparatus, machinery, plant and equipment to the photomicrography of tissues, mineral sections, metal surfaces and the applications of the wet plate and

Lumière color plate. Photo-engraving is a branch by itself full of the most elaborate and intricate details and also full of possibilities in the line of more perfect development. The moral of all this is that the chemist and technologist will find it to their advantage to be photographers. Some institutions of learning include photography among their courses. But the curricula are already generally full and until some general agreement as to what is most advisable in the curriculum for the education of a chemical engineer, we do not advise adding photography to the courses of study. What we do advise, is, if it is not advantageous or expedient to take a course in photography, that each man take it up for himself. It will be found one of the most fascinating and profitable avocations which could possibly be undertaken. We recommend further that the study be not taken up piecemeal, haphazard, irregularly, or in a dilettante spirit. Let the amateur cover the whole ground of cameras, lenses, diaphragms, shutters, exposures, wet and dry plates, developers and prints! There be photographs without pith or merit, smudgy, cloudy, distorted and out of focus which could well be spared by many an editor and printer. It were well to eliminate these altogether. The technical or scientific photograph, which is clean cut, detailed, properly lighted and properly developed and printed, is a joy to the engraver, printer and beholder.

## ORIGINAL PAPERS.

THE ACTION OF SUNLIGHT AND AIR UPON  
SOME LUBRICATING OILS.

By C. E. WATERS.

Received October 1, 1910.

In 1885, Schaal<sup>1</sup> patented a process for the manufacture of soaps by the action of air upon mineral oils in the presence of alkaline substances. This was based on an earlier observation of Engler's.

In 1891, Zaloziecki<sup>2</sup> studied the oxidation of petroleum by means of air. By blowing cold air through the oil the oxidation was slight, but was greatly increased in the presence of sodium hydroxide. The acidity shown by methyl orange, as opposed to phenolphthalein, he believed to be due to the oxidation of mercaptans and organic sulphides, and not to traces of the acid used in the refining.

Schestopal<sup>3</sup> found that illuminating oils absorbed several volumes of oxygen at room temperature, when enclosed in sealed tubes laid horizontally. He pointed out the bearing this had upon the treatment of kerosene in agitators.

<sup>1</sup> D. R. P. 32,705. *Chem.-Zig.*, 9, 1520 (1885).<sup>2</sup> *Z. angew. Chem.*, 1891, 416-9.<sup>3</sup> *Chem.-Zig.* 18, 352-4 (1895).



Holde<sup>1</sup> exposed mineral and vegetable oils to the air for a long time, studying changes in viscosity, specific gravity, etc. He found that the changes were much less for mineral than for vegetable oils.

Haack<sup>2</sup> believed that the oxidation observed in refining oils was due to the combined action of concentrated sulphuric acid and air. This idea was upheld by Kern.<sup>3</sup> Other papers bearing upon the question of oxidation by atmospheric oxygen were published.<sup>4</sup>

Zaloziecki<sup>5</sup> studied the influence of light and air upon the acid treatment of kerosene. In some of his experiments he used colored glass. The general conclusion reached by him was that light and air should be excluded. Ostrejko<sup>6</sup> confirmed this work as to the effect on the color of refined petroleum, and also determined the increase in acidity due to oxidation. Wischin<sup>7</sup> thought that the darkening in color of kerosene was perhaps due to a molecular rearrangement of dissolved asphalt under the influence of actinic rays.

Hirsch<sup>8</sup> passed air through mineral oils in the presence of soda lye and, even after 12 hours at 70°, could detect no change in the alkali, concluding from this that there was no oxidation. Aismann<sup>9</sup> found that the absorption of oxygen was very slight. It was also stated by Künkler and Schwedholm<sup>10</sup> that there was no increase in weight when mixtures of mineral oil with bone oil, olive oil, etc., were rubbed up with sand or pumice and exposed to the air. The resinification noticed was believed to be due solely to polymerization.

There can be no doubt, however, that oxidation really takes place. Charitschkow,<sup>11</sup> who states that the resinous products formed in petroleum on long standing under the combined influence of light, air and moisture are nearly identical with those of Schaal, obtained sirup-like acids<sup>12</sup> by the action of air in the presence of alkalis. These acids, which are nearly insoluble in benzene and petroleum ether, he calls "polynaphthene" or "asphaltogenic" acids, the latter name being self-explanatory. Meyerheim,<sup>13</sup> in this connection, thinks the increase in asphalt with lapse of time is due to polymerization or to a change from the original colloidal state to the insoluble condition. His experiments were carried out in closed bottles, two-thirds filled with oil. The changes in asphalt content in two oils, kept in the dark, in diffused light and

under the influence of radium emanations, were determined. After 8 months no difference due to the action of radium could be detected. In diffused light one oil showed a higher asphalt content than a control kept in the dark; the other oil showed a somewhat higher content of asphalt in diffused light.

Molinari and Fenaroli<sup>1</sup> obtained unstable ozonides from petroleum hydrocarbons. They were precipitated from their solutions in benzene, ether or chloroform by means of petroleum ether. They decomposed at 20°, changing at 35–50° into a soft, red substance which was converted into a resinous mass at 105°.

An interesting observation bearing on the work described in this paper was made by Ackerman.<sup>1</sup> A sample of naphtha from Russian Turkestan was entirely thickened on exposure to the sun's heat for a whole year in an open vessel. Fresh samples of naphtha yielded 76.68 per cent. of distillate between 20° and 310°, while the thickened oil yielded only 15.67 per cent. of distillate.

In a paper entitled "Studies on the Carbenes," Mackenzie<sup>2</sup> shows that the action of light upon solutions of asphalt in carbon tetrachloride greatly increases the percentages of "carbenes" or insoluble bitumens. This is shown to be due to the formation of hydrochloric acid, which precipitates the carbenes.

The present writer was at the time determining asphaltic material in certain lubricating oils, and the above-mentioned paper, though on a somewhat remotely related subject, suggested the experiments herein described.

Three samples of oil were used. B and C were straight mineral oils; B was moderately dark in color, while C was much lighter colored and less viscous. D resembled B in color and viscosity, but contained approximately 0.5 per cent. of fatty oil.

Duplicate samples of 20 grams each were weighed into 150 cc. Erlenmeyer flasks, loosely covered with caps to exclude dust and rain, and were exposed outside a window facing south for 23 days. Within 2 or 3 days the samples began to show a slight cloudiness, and after a week or ten days the insoluble matter formed a cake on the bottom. After 23 days the contents of each flask were diluted with 50 cc. of ligroin and after 36 hours the insoluble matter was filtered off in Gooch crucibles, washed with ligroin, dried at 100° and weighed. The following percentages of insoluble matter were found:

Sample.	B.	B.	C.	C.	D.	D.
Insoluble per cent. ....	0.77	1.03	2.42	2.86	1.40	1.91

The discrepancies between duplicate samples are believed to be due to their having received unequal amounts of sunlight, as it was necessary to place the flasks in a crystallizing dish to prevent their blowing

<sup>1</sup> Mith. kgl. techn. Versuchsanst., **10**, 85–90 (1892); *J. Soc. Chem. Ind.*, **11**, 619 (1892).

<sup>2</sup> *Chem.-Ztg.*, **16**, 694 (1892).

<sup>3</sup> *Ibid.*, **17**, 706 (1893).

<sup>4</sup> Zaloziecki, *Chem.-Ztg.*, **16**, 591 (1892). Holde, *Ibid.*, **18**, 794, 1737

1835 (1894). Hirsch, *Ibid.*, **18**, 1824.

<sup>5</sup> *Ibid.*, **19**, 875–7, 956–8 (1895).

<sup>6</sup> *J. Soc. Chem. Ind.*, **16**, 345 (1896).

<sup>7</sup> *Chem. Rev. Fett-Harz-Ind.*, **1895**, Nos. 26 and 27; *J. Soc. Chem. Ind.*, **14**, 1039 (1895).

<sup>8</sup> *Chem.-Ztg.*, **19**, 41 (1895).

<sup>9</sup> *Dingl. pol. J.*, **294**, 658 (1894); *J. Soc. Chem. Ind.*, **14**, 282 (1895).

<sup>10</sup> *Seifenindustrieztg.*, **35**, 341; *Chem.-Zentr.*, **1908**, I, 1859.

<sup>11</sup> *Z. angew. Chem.*, **21**, 1155 (1908).

<sup>12</sup> *Chem.-Ztg.*, **33**, 1165 (1909).

<sup>13</sup> *Ibid.*, **34**, 454 (1910).

<sup>1</sup> *Ber.*, **41**, 3704 (1908).

<sup>2</sup> *This Journal*, **2**, 124–7 (1910).

away, and late in the afternoon those outside were in the sun longer than the others.

Another test was then started with approximately 10 gram samples, the flasks being weighed at intervals. After each weighing the flasks which showed the least gain were placed so as to receive the maximum of sunlight. For this reason the last figures given in the next table are more concordant than they would otherwise have been.

Sample.	B.	B.	C.	C.	D.	D.
Weight of oil.....	10.002	10.012	10.025	10.023	10.023	10.003
Total gain after:						
31 days (gram).....	0.176	0.152	0.187	0.183	0.154	0.139
46 days (gram).....	0.192	0.174	0.215	0.207	0.176	0.159
80 days (gram).....	0.233	0.223	0.274	0.278	0.221	0.201
110 days (gram).....	0.277	0.263	0.327	0.340	0.274	0.243
132 days (gram).....	0.290	0.289	0.358	0.369	0.297	0.268

That the increase in weight is somewhat influenced by the temperature and is not entirely due to rays of short wave length, seems clear from the results obtained when two lots of oil B were exposed in very shallow dishes made by cutting off the bottoms of two beakers of the same diameter. One was covered with a thick watch-glass. The other was uncovered and so shallow that hardly any light passed through glass before falling on the oil.

Dish.	Uncovered.	Covered.
Weight of oil.....	10.001	10.001
Gain after 6 hrs., bright sun (gram).....	0.0354	0.0354
Further gain after 6 hrs., bright sun.....	0.0183	0.0198
Further gain after 6 hrs., bright sun.....	0.0154	0.0179
Further gain after 6 hrs., partly cloudy.....	0.0085	0.0094
Further gain after 4 hrs., partly cloudy.....	0.0050	0.0061
Further gain after 6 hrs., dull $\frac{1}{2}$ of time.....	0.0059	0.0068
Further gain after 6 hrs., dull $\frac{1}{3}$ of time.....	0.0063	0.0071
Further gain after 6 hrs., dull $\frac{1}{2}$ of time.....	0.0049	0.0065
Total gain (gram).....	0.0997	0.1090

In the cool, windy weather then prevailing, the oil in the covered dish must have been warmer than that in the uncovered one. On the first five days the dishes rested on white paper. This was replaced by black paper on the last three days, but only a slight change in the results was noticed. The increasing opacity of the oil due to the formation of insoluble matter and the increasing saturation with oxygen would both tend to mask any effect due to a slight rise in temperature. Traces of precipitate were noticed at the end of the first six hours.

The observed increase in the weight does not truly represent the amount of oxygen involved, for carbon dioxide, water and volatile organic matter are lost. Twenty-five grams of oil B were exposed in a flask having a glass stopper with sealed-in tubes so that a slow current of purified air could be passed over the surface of the oil, carrying the carbon dioxide into baryta water. In seven days, only three of which were sunny, 0.0249 gram of carbon dioxide was found. On exposing the same sample for seven days longer, about four and a half of which were sunny, there was the further formation of 0.0223 gram of carbon dioxide.

In a final experiment, the oil was exposed in an

Erlenmeyer flask with glass stopper and delivery tubes. The water formed was carried by a slow current of dry air, passing over the surface of the oil, into a calcium chloride tube and finally weighed. It was noticed that the calcium chloride where the air entered was stained yellow, and that there was a whitish coating on the inside of the tube leading in through the window from the flask. Evidently some organic matter was given off. The carbon dioxide was absorbed in baryta water as before, finally set free by dilute hydrochloric acid, absorbed in a potash-bulb and weighed. The change in weight of the oil was also determined as well as the amount of insoluble oxidation product.

The following data were obtained after 22 days constant exposure on the window-sill:

	Per cent.
Gain in weight of oil.....	1.83
Water formed (corr. for $H_2O$ in oil).....	0.89
Carbon dioxide.....	0.37
Total.....	3.09
Oxidation product.....	1.47

The figures for water and gain in weight of the oil are slightly in error on account of the volatile oil matter mentioned. However, the total of 3.09 per cent. agrees closely with the figure 2.89 per cent., obtained by adding the gain in weight of the oil to the oxygen in the water and carbon dioxide found.

The "insoluble" oxidation product dissolves to only a slight extent in ligroin. It is readily filtered on a Gooch crucible, and when washed with ligroin and dried is a light brown powder. It dissolves in strong alcohol and more easily in dilute alcoholic potash and in ether. Attempts to crystallize it and to obtain a crystalline potassium salt were fruitless.

The amount found evidently accounts for only a small part of the 1.83 per cent. of oxygen taken up by the oil. The following analyses show that a large part of it remains in solution in the oil, or that most of the oil is too slightly oxidized to form the insoluble product.

Found.	C.		H.		O.	
Original oil.....	86.40	86.34	13.83	13.63	19.30	19.61
Oxidation product.....	72.87	72.58	7.83	7.81	7.30	7.30
Oil filtered off.....	84.55	84.44	13.45	13.38	2.00	2.18

To determine changes in the acidity of the oils, 20-gram samples of each were exposed, in duplicate, for 23 days. After dilution with benzene, they were titrated with  $N/10$  alkali, the results being calculated as percentages of oleic acid.

Sample.	B.	B.	C.	C.	D.	D.
Acidity of original oil.....	0.08	0.08	0.03	0.03	0.07	0.07
Acidity after exposure.....	3.66	3.75	3.29	3.30	3.00	..

Attempts to obtain concordant figures for the permanganate value of the oil were fruitless, as the permanganate was decomposed catalytically, no true end-point being obtained. The oils were shaken with dilute sulphuric acid and heated on the steam-bath,

standardized permanganate being added from time to time. Apparently the temperature was too high, for it has been shown quite recently by Sarkar and Dutta<sup>1</sup> that at or above 81°, permanganate is decomposed by manganous sulphate, with formation of manganese peroxide, even in the presence of considerable sulphuric acid.

BUREAU OF STANDARDS,  
September 29, 1910.

## COMPARATIVE ANALYSES OF WATER FROM GREAT SALT LAKE.

By W. C. EBAUGH and WALLACE MACFARLANE.

Received September 5, 1910.

From about 1900 until 1904 fears were expressed that the Great Salt Lake was doomed to extinction, and that it would be a matter of only a few years until its site would become a salt desert. The recession of the shore line and sinking of the lake level continued until the autumn of 1903. Since that time there has been a rise in the level of the lake, and during the year just ending new fears have arisen—fears that large engineering works like the Lucin cut-off of the Southern Pacific and the roadbed of the Western Pacific railroad would have to be abandoned. A succession of years with abnormally high rainfall is responsible for the condition now existing.

TABLE I.

	Date of collection.	Specific gravity.	Total solids, Per cent. by weight.	Grams per liter.	Authority.
	1850	1.170	22.282	260.69	L. D. Gale
Summer,	1869	1.111	14.9934	166.57	O. D. Allen
Aug.,	1873	1.102	13.42	147.88	H. Bassett
Dec.,	1885	1.1225	16.7162	187.65	J. E. Talmage
Feb.,	1888	1.1261			J. E. Talmage
June,	1889	1.148			J. E. Talmage
Aug.,	1889	1.1569	19.5576	226.263	J. E. Talmage
Aug.,	1892	1.156	20.51	238.12	E. Waller
Sept.,	1892	1.1679	21.47	250.75	J. E. Talmage
	1893		20.08		J. T. Kingsbury
Dec.,	1894	1.1538	21.16	244.144	J. E. Talmage
May,	1895	1.1583	21.39	247.760	J. E. Talmage
June,	1900	1.1576	20.90	241.98	H. N. McCoy and Thos. Hadley
July,	1900	1.1711	22.89	268.09	H. W. Shiley
Aug.,	1900	1.1805	23.36	275.765	H. W. Shiley
Oct.,	1900	1.1860	24.03	285.020	H. W. Shiley
Sept.,	1901	1.1979	25.221	302.122	L. J. Seckles
Oct.,	1903	1.2206	27.72	338.36	Wm. Blum
June,	1904	1.2105	25.196	299.96	J. E. Talmage
Nov.,	1904	1.2120	26.71	323.71	Wm. Blum
Oct.,	1905	1.1810	22.92	270.985	W. C. Ebaugh and Kenneth Williams
Oct.,	1909	1.1561	20.887	242.25	Wallace MacFarlane
Feb.,	1910	1.1331	17.681	200.32	Wallace MacFarlane

NOTE.—The above values are taken in part from "The Great Salt Lake," by J. B. Talmage, and all the analyses during recent years have been made in the laboratories of the University of Utah.

An inspection of the results of analyses of the lake water will be of interest. In Table I are shown the specific gravity and total solids obtained by investigators at various times during the last forty or more years, and in Table II more complete results of the latest analyses are recorded. In this connection it should be remembered that the annual variation

of the lake water shows a minimum of total solids in the spring, following the winter and spring precipitation, and a maximum in the autumn.

TABLE II.

Sample collected.....	Oct., 1903	Nov., 1904	Oct., 1907	Oct., 1909	Feb., 1910
Specific gravity.....	1.2206	1.2120	1.1810	1.1561	1.1331
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids.....	27.72	26.71	22.92	20.88	17.68
Constituents.					
Chlorine (Cl).....	15.27	14.54	12.67	10.91	9.48
Sulphate (SO <sub>4</sub> ).....	1.86	1.82	1.53	1.39	1.05
Magnesium (Mg).....	0.155	0.43	0.45	0.447	0.391
Calcium (Ca).....	0.045	0.055	0.04	0.080	0.055
Sodium (Na).....	9.58	8.77	7.88	7.25	5.79
Potassium (K).....	0.73	0.89	0.72	0.76	0.88

UNIV. OF UTAH,  
SALT LAKE CITY.

[CONTRIBUTION FROM THE TEXAS AGRICULTURAL EXPERIMENT STATION.]

## CONSTITUENTS OF CANDELILLA WAX.

By G. S. FRAPS and J. R. RATHER.

Received September 16, 1910.

The wax is from the Candelilla, or Mexican wax plant, which grows in a number of Mexican states. The sample was secured for us by Dr. H. H. Harrington, Director of the Texas Experiment Station. It is a hard wax, opaque, and almost colorless. A description and constants of this wax have been given by Hare and Bjerregaard.<sup>1</sup> According to an editorial in the *Journal of the Royal Society of Arts*,<sup>2</sup> the following uses have been suggested for it; candles, shoe polish, phonographic records, insulation of electric wires, and as a bees' wax substitute.

**Constants.**—The following constants were determined by A. C. Deiler in the spring of 1909. For the sake of comparison, the same constants as ordinarily secured for bees' wax are given, and also those obtained by Hare and Bjerregaard.<sup>3</sup>

	Candelilla wax.		
	Deiler.	Hare	Bees' wax.
Specific gravity at 100° C.	0.870	....	....
Specific gravity at 15–15° C.	....	0.9825	....
Iodine number.....	14.0	36.8	6–13
Acid number.....	19.0	12.4	19–21
Ester number.....	40.7	....	73–76
Saponification number.....	59.7	64.9	....
Melting point.....	66° C.	67–8° C.	....
Unsaponifiable matter, per cent. ....	....	91.17	....

Our sample of wax was completely soluble in chloroform and carbon bisulphide. Ether dissolved 0.12 gram in 100 cc. and alcohol 0.048 gram, wax and solvent being brought together for fifteen minutes at room temperature.

**Isolation of a Hydrocarbon.**—The wax was powdered and saponified with alcoholic potash and the alcohol evaporated off. It was then transferred to a Kutscher and Steudel extraction apparatus with hot water and extracted with ether. After extracting

<sup>1</sup> THIS JOURNAL, 2, 204 (1910).

<sup>2</sup> 57, 644

<sup>3</sup> Loc. cit.



for 40 hours (5 days) the extract was washed twice with water and evaporated to dryness. About 40 per cent. of the wax was extracted. The extract was dissolved in hot ether, cooled, and allowed to crystallize. The crystals were washed on a filter paper with cold ether; the mother liquid and washings were evaporated to dryness. The crystals were recrystallized from ether three times. Both crystals and residue from mother liquor then had a melting point of 68° C. The crystals were recrystallized from chloroform and melted at 68° C. The mother liquid, on evaporation to dryness, left a residue which melted at the same temperature. This was taken to indicate the purity of the product.

The substance appears as fine white crystals. It is readily soluble in hot ether, fairly soluble in cold ether, insoluble in cold 95 per cent. alcohol and slightly soluble when heated. It is soluble in cold carbon tetrachloride. It is more easily soluble in chloroform than in ether.

A small portion of the substance was distilled and the solidified material had the same melting point as the original substance.

Tested by Hell's method,<sup>1</sup> by heating with soda lime, the sample did not appear to be an alcohol. This substance appears to be the hydrocarbon hentriacontane, which is found also in bees' wax.

Analyses gave the following results:

	Calculated for $C_{30}H_{62}$ Per cent.	Found.
Carbon.....	85.30	85.48 85.16
Hydrogen.....	14.70	14.10-14.28

**Other Substances.**—The mother liquors from the above hydrocarbon were combined, recrystallized from ether and then heated with 95 per cent. alcohol, filtered, allowed to cool, and filtered again. The alcohol was evaporated off and the resulting solid dissolved in ether. On evaporation no crystals separated out. The product is a transparent, yellowish, resinous, solid—brittle when dry and melting at 55° C. It is readily soluble in cold ether and alcohol. It was evidently not completely pure. This substance is not a hydrocarbon, but contains oxygen. Tested by Hell's method, it gave practically no gas (0.12 per cent.), and we believe this gas to be hydrocarbon produced by the cracking of the substance, and not hydrogen. This substance, therefore, does not appear to be of alcoholic nature.

Analysis gives the following results:

	Per cent.
Carbon.....	83.85
Hydrogen.....	12.33

After extracting the original material with ether for 40 hours it was salted out and extracted with boiling ether. About 30 per cent. of the original substance was secured. The product was recrystal-

lized from ether four times. This product was heated with alcohol and filtered hot. The filtrate was evaporated to dryness and the product recrystallized twice from alcohol and three times from ether.

The resulting solid was a shining, white crystalline substance, very similar to the hydrocarbon first mentioned, but more easily soluble in alcohol. It is slightly soluble in cold ether, more soluble in hot ether. It melts at 85° and is probably a hydrocarbon.

From the mother liquor we secured further quantities of the hydrocarbon melting at 68° C. Other substances are also present in this wax, and it is our intention to investigate it further, but we are at present unable to do so.

#### SUMMARY.

Candelilla contains a hydrocarbon hentriacontane melting at 68°, and probably one melting at 85°. It also contains other substances.

### AN EXTRACTION APPARATUS.

By SAMUEL M. BAIN.

Received August 25, 1910.

In connection with cotton breeding experiments for the U. S. Department of Agriculture, the writer has for several years been studying the oil content of the cotton seed as an hereditary factor, and has developed an outfit for extraction with ether which has after long use proved very efficient.

Fig. 1 shows a general view of the apparatus resting on the small table support. The heating device is essentially that described by Hopkins.<sup>1</sup> It consists of a wooden base provided with connections for five 32 c. p. incandescent globes, with a double-walled

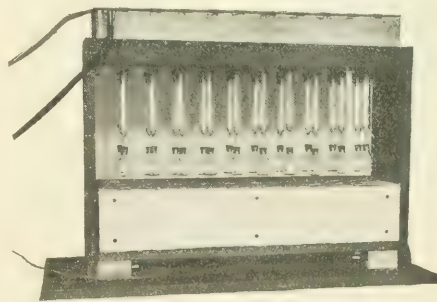


Fig. 1.

galvanized iron box, fitted with lid carrying 20 holes serving as rests for 20 extraction flasks. In addition to the asbestos packing between the double vertical walls of this box, as recommended by Hopkins, it was found desirable also to cover the sides with heavy asbestos sheeting, and to apply a thinner asbestos

<sup>1</sup> *Ann. Chem. (Liebig)*, **223**, 269.

<sup>1</sup> *J. Am. Chem. Soc.*, **21**, 645 (1899).

cover with holes corresponding to those in the galvanized iron lid. This heater rests, as shown in the figure, on two blocks 5.8 x 10.5 x 23.5 cm. By lifting the heater, which moves freely between the ends of the upright stand, and turning these blocks edgewise, the flasks come into position over the holes in the lid.

At the top of the stand is a galvanized iron box 16 x 23.3 x 97.8 cm., into which are soldered the condenser worms in proper position over the flasks. The worms are made of block-tin tubing (6.5 mm. inside) and make two coils each within the box. Each pair of worms is braced across the top of the box with galvanized iron strips 2.8 cm. wide and projects below 7.5 cm. to a beveled end, as shown in detail in Fig. 2.



Fig. 2.

The worms are kept cool by a current of water flowing through the box, the inflow being led by a lead pipe to the bottom and at the extreme right of the box, the exit taking place at the left, as shown in Fig. 1. For convenience in moving about the room, the worm tubes should pass through the braces and extend 2 or 3 cm. above the top of the box, and the box should be made 2 or 3 cm. deeper than the dimensions above indicated. This would permit the location of the off-flow pipe at a sufficient distance below the rim of the box to prevent the tipping over of water on moving the apparatus.

The support tubes are shown in detail in Fig. 2, and are of a well-known pattern. They are, however, shown longer than they should be, the illustration being of a type made to fit another pattern of sample tube. The dimensions of these tubes should therefore be: body of tube, 2.8 cm. inside diameter, 15.3 cm. long; stem, 7.5 mm. outside, 9 cm. long.

The greatest difficulty connected with this type of extraction apparatus is the requirement of cork stoppers, and the writer at first experienced much difficulty in this direction. A method of fitting them was, however, finally devised which overcomes nearly all the inconveniences of the cork stopper. In the first place, a large stock of corks of the best obtainable quality should be available from which those best suited to the purpose may be chosen. By plunging for two or three minutes in vigorously boiling water, a cork softens and may with a little care be forced while still hot and wet into a comparatively

small tube or neck. If allowed to remain for a few hours in this tube, then withdrawn two or three millimeters at a time at intervals extending over several days, the cork is molded, so to speak, to fit its tube. It has then a gradual slope from its smaller end fitting the tube, and may be forced further as required. This fitting should be done before the hole is bored for adjusting on the worm tube. After the cork has dried in its tube the hole should be bored a little smaller than the tube it is to fit, and before adjusting to this tube a jet of steam is allowed to pass through the hole and the cork at once forced over the worm tube, the cork meanwhile remaining in position in the glass tube. This is then allowed to dry a few days as in the former case.

In a similar way the corks are fitted to the flasks below, as shown in Fig. 2. After drying, the apparatus is set in operation and ether allowed to play upon the corks for a day or two, so as to remove all their readily soluble constituents. If any leaks occur, as will be indicated by loss of ether or by extracted soluble material accumulated around holes on the exposed surfaces of the corks, defective ones are replaced as before.

In order to facilitate the replacement of parts accidentally broken, it is important to have each flask neck and each part of the extraction tube forming a cork connection made uniform in size and perfectly cylindrical. This means that a cork fitting one connection of a set will fit all the others.

Another difficulty to be overcome in using tightly fitted corks is the occasional cracking of the tubes due to sudden changes in temperature and the non-yielding qualities of the cork. This can be largely overcome by leaving the connections somewhat loose until the corks are wet and softened by the warm, freshly condensed ether. At the close of an experiment it is also well to disconnect the parts before the corks have dried out. To avoid the effect of air currents it is wise to cover the apparatus while in use. When a good quality of glass is used and these precautions are taken, very few tubes are broken.

The most distinctive feature of this apparatus is the combined weighing and extraction tube shown in Fig. 3. It consists of four parts: (1) The upper cap, ground on the outside of the body of the tube;

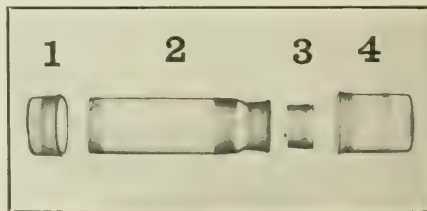


Fig. 3.

(2) the body of the tube 25 x 75 mm. narrowed to a neck, as shown; (3) a hollow cone ground to fit the neck and squared at either end, diameter at small end 18.5 mm., length 12 mm.; (4) lower cap ground to fit on outside of body of tube as shown, outside diameter of flared part 27 mm., length 32 mm. Extreme length of tube with caps, 90 mm.

In use a disk of filter paper 21.5 mm. diameter (C. S. & S. "Blue Label" gave best results) is wet with distilled water, centered on the small end of the cone, and carefully forced into the neck. The whole is then placed in the oven to dry, and after drying, the cone readjusted to take up the shrinkage of the paper, and the caps replaced. The tube is then weighed and the sample poured in and weight of sample obtained by difference. The whole is now put into the oven and dried, in which operation the caps are both removed and the tube allowed to stand on end, the cone serving as base. The writer uses a copper tray 26 x 193 x 226 mm., divided into 12 partitions, which serves to carry twelve tubes with their caps, each set by itself. After drying, the caps are replaced and the dry weight obtained. The caps are now removed and the tube carrying the sample placed in position for extraction, as shown in Fig. 2, resting on a copper wire.

After extraction the filtrate may be weighed directly in the flask below, or the caps may be replaced after driving off the ether and the tube containing the residue weighed.

In Fig. 2 is shown a sealed glass bob containing a bit of iron wire suspended within the extraction tube and attached to the end of the tin tube by means of a silk cord. This leads the condensed ether down near to the sample and prevents spattering. If by accident any of the sample has become attached to the wall of the tube, a magnet applied to that side will pull this bob over and cause the ether to run down the wall over the adhering bit of sample. By attaching a few short, loose strands of silk cord to this bob it may be made to adhere permanently to any desired portion of the tube. There is, however, seldom need of directing the ether current down the wall, for the ether soon accumulates for 30 or 40 mm. above the sample and remains constantly at this level. Of course, the rate of ether distillation may be controlled at will. This combined weighing and extraction tube <sup>1</sup> has been in use in the writer's laboratory for about a year, and has proved entirely satisfactory. The advantages in its favor are:

(1) The sample may be directly weighed, the moisture taken, the extraction made, and all necessary manipulations carried out without transfer of sample.

(2) Owing to the perfect fit of the filter joint, the extract comes through quite clear.

(3) All manipulations are quite simple, and considerable time is saved as compared with the use of the prevailing forms of extraction apparatus.

(4) By properly regulating the rate of ether distillation the sample is kept constantly covered with the solvent.

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## CONTRIBUTION ON JELLY-MAKING.

(SECOND PAPER.)

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Received August 30, 1910.

The previous report<sup>1</sup> founded upon experiments with fall fruit juices established the following general results: The essential constituents of fruit juices suitable for jellies are pectin and acid. A desirable accessory in jelly-making is cane sugar. Too much sugar causes deterioration of the quality of the jelly. Over-dilution of fruit juices is a frequent cause of the use of too much sugar. The physical constants of jellies ready to jell are practically, boiling point 103° C. and specific gravity 1.28. Jelly-making is so controlling conditions by means of acid and sugar that the pectin of the fruit juices may be precipitated evenly throughout the volume allotted to it.

The present report embraces some work on apple and quince juices, also such summer fruits as currant, raspberry, strawberry, blackberry, blueberry and cherry, and in general it strengthens the preceding conclusions.

*Extraction of Juices from Fruits.*—The juices of these summer fruits were extracted, in most cases, by adding to four or five quarts of the prepared fruit the least possible amount of distilled water (perhaps 200 cc.) just enough to prevent burning, then simmering very slowly, mashing, and finally draining through double cheesecloth. These first juice extractions then, unlike most of the fall fruits, were very nearly undiluted material. Further juice extractions were made by slowly cooking up the remaining pulp with a relatively large supply of distilled water, then draining as before. Although several such extractions with any given pulp were made, yet the alcohol test always proved that the limit of pectin extraction had not been reached; however, the proportion of it present was constantly diminished. From an economic standpoint, perhaps, it is not always practical to use the last very dilute extractions for jelly, although scientifically it would be interesting to ascertain the limit of pectin in various fruit pulps. Juices extracted as described were heated to boiling, sealed into fruit jars, and kept for future experiments.

*Proportion of Sugar to Juice.*—An effort was made

<sup>1</sup> The writer wishes to acknowledge his indebtedness to Mr. H. H. Hampton, late assistant chemist of the Tennessee Experiment Station, for valuable suggestions in developing this tube.

<sup>1</sup> THIS JOURNAL, I, 333.



to discover a relationship between the specific gravity of juices and the quantity of sugar they can utilize in jelly-making. That such a relation does exist for a given juice in hand seemed probable from the results obtained, but these results did not indicate such a relationship between the juices of different fruits. Juices of different fruits (and even of the same fruit), apparently, are too variable in composition, depending upon acidity and proportion of solids present—due in part to the method of extraction and perhaps also to the condition of the fruit when used. If fruit juices were acid solutions of pectin alone, *i. e.*, contain no admixture of other solutes, probably the relation sought would be found to exist.

TABLE I.

No.	Kind.	Sp. gr. of juice	Percent of acid calculated as $H_2SO_4$	Vol. of sugar to 1 vol. of juice	Time of boiling juice (min.)	Texture of jelly.	
						Refractive index of jelly shown by opening-angle.	Texture of jelly.
190	Sour apple	1.042	0.860	1/2 : 1 15	20		Tough
191		1.042	0.860	3/4 : 1 15	15		Excellent
192		1.042	0.860	1 : 1 15	12		Slightly soft
193		1.042	0.860	1 1/2 : 1 15	8		Very soft
194		1.042	0.860	2 : 1 15	4		Pectin pptd. in lumps.
21	Currant <sup>1</sup>	1.038	1.892	1/2 : 1 10	3		Tough
20		1.038	1.892	3/4 : 1 10	2		Excellent
22		1.038	1.892	1 : 1 10	1		Very good
23		1.038	1.892	1 1/2 : 1 10	1		Soft
24		1.038	1.892	2 : 1 10	4		Gummy and soft
311	Blueberry	1.020	0.483	1/4 : 1 10	15		Tough
310		1.055	1.332	3/4 : 1 2	6		Excellent
314		1.055	1.332	1 : 1 2	5		Good
313		1.055	1.332	1 1/2 : 1 ..	..		Soft
281	Red rasp- berry	1.048	1.809	3/4 : 1 15	20		Excellent
280		1.048	1.809	1 : 1 15	10		Soft
292	Blackberry	1.050	1.208	3/4 : 1 15	12		Excellent
291		1.050	1.208	1 : 1 15	5		Soft

a quantity greater than the pectin of the juice can utilize. The preceding record shows some results of experiments having as their object the determination of the amount of sugar preferable for the various juices.

Examination of this table emphasizes the following facts: With increasing proportion of sugar, the time necessary for boiling decreases, the volume of jelly increases, while the texture of the jelly constantly changes from tough to a condition so soft that it will not hold together. Fig. 1 shows photographs of samples of 191, 192, 194. In general, with juices of specific gravity and acidity here considered, a three-fourths volume of sugar to one of juice was preferable, though currants and blueberries yielded jellies of good texture when the proportion of sugar to juice by volume was 1:1. Unquestionably, in the ordinary practice of jelly-making much depends upon the proportion of water added to extract the juice from the fruit, and probably something depends upon the condition of the fruit when used. In any case, too little rather than too much sugar should be the rule in jelly-making. A superabundance of sugar leads to a crystallization of sugar throughout the whole mass. Samples of 194 and 24 within a month from making were filled with large crystals.

*Inversion of Sugar in Jelly-making.*—Considerable further work has been done to determine the proportion of sugar inversion preferable in jelly-making. For this purpose jellies were made from blueberry, currant, red raspberry, blackberry, apple, quince, and plum juices—the general method of procedure being as follows: After having determined the proportion of sugar to use, then three samples of each jelly were made, the first having juice and sugar cooked together from start to finish, the second having the



See Nos. 191, 192, and 194, Table I.

Fig. 1

Continued experiments proved beyond question that a most frequent cause of failure in jelly-making lies in the use of an over-abundance of sugar,<sup>2</sup> *i. e.*,

sugar added (hot) so that juice and sugar should boil together about one-half the total time of cooking, and the third having the hot sugar so added that the two should be cooked together from two to four minutes only. The results are tabulated in Table II:

<sup>1</sup> Expts. done by Miss Grace Stevens.<sup>2</sup> This JOURNAL, I, 336.

TABLE II.

No. of experiment.	Kind of fruit.	Sp. gr. of juice.	Per cent. of acid in juice calc. as sucrose.	No. of juice extractions.	Wt. of juice (gramm).	Prop. tion of cane sugar in juice (by vol.).	Wt. of cane sugar (g.).	Time of boiling (min.).	Before adding sugar.	After adding sugar.	Temp. at which jelly-test was observed.	Wt. of jelly (grams).	Wt. of skimmings (grams).	Wt. of jelly and skimmings (grams).	Per cent. of cane sugar put into jelly.	Before inversion.	After inversion.	Temp. at which jelly-test was observed.	Per cent. of cane sugar in jelly.	Per cent. of cane sugar in fruit.	Per cent. of cane sugar in juice.	Per cent. of cane sugar in jelly.
400	Blueberry	1.065 1.332	I	214	1	1165.6	5	12	102°	102°	297.5	21.0	318.5	52.00	12.54	- 9.90	22°	33.75	64.90	35.10		
401		1.065 1.332	I	214	1	1165.6	5	5	102°	102°	312.5	5.0	319.5	52.00	18.40	-12.10	21°	45.69	87.67	12.33		
402		1.065 1.332	I	214	1	1165.6	8	2	102°	102°	303.0	6.0	309.0	53.00	21.80	-10.30	22°	48.27	91.07	8.93		
403	Blueberry	1.039 0.962	II	211 3/4	1	1124.2	0	15	102°	102°	228.5	22.0	250.5	51.64	15.00	- 9.70	23°	37.28	72.19	27.81		
404		1.039 0.962	II	211 3/4	1	1124.2	8	7	102°	102°	239.7	16.5	256.2	48.08	17.60	- 9.20	22°	40.30	83.81	16.18		
405		1.039 0.962	II	211 3/4	1	1124.2	13	2	102°	102°	240.5	15.0	255.5	48.61	20.90	- 9.70	23°	46.18	95.00	5.00		
406	Currant	1.045 2.417	I	210 3/4	1	1124.2	0	17	103°	103°	211.3	23.0	234.3	53.00	4.00	-10.00	25°	21.29	40.17	59.83		
407		1.045 2.417	I	210 3/4	1	1124.2	9	8	103°	103°	215.5	16.0	231.5	53.65	11.20	-10.00	26°	32.36	60.31	39.69		
408		1.045 2.417	I	210 3/4	1	1124.2	15	2	103°	103°	223.0	9.0	232.0	53.53	20.55	-11.20	18°	47.03	87.85	12.15		
409	Red rasp- berry	1.047 1.809	I	262 3/4	1	1187.5	0	19	103°	103°	320.8	18.9	339.7	55.19	9.00	-10.55	18°	29.00	52.54	47.46		
410		1.047 1.809	I	262 3/4	1	1187.5	10	9	103°	103°	322.0	12.5	334.5	56.02	16.50	-11.00	18°	40.74	72.72	27.28		
411		1.047 1.809	I	262 3/4	1	1187.5	15	4	103°	103°	319.0	8.7	327.7	57.21	21.40	-10.50	19°	47.43	90.84	9.16		
412	Black- berry	1.051 1.208	II	262 3/4	1	1187.5	0	28	103°	103°	304.5	19.0	323.5	58.00	16.00	-11.00	19°	40.00	69.00	31.00		
413		1.051 1.208	II	262 3/4	1	1187.5	18	10	103°	103°	298.0	18.0	316.0	59.00	24.30	-12.10	19°	54.12	91.73	8.27		
414		1.051 1.208	II	262 3/4	1	1187.5	25	2	103°	103°	306.0	10.0	316.0	59.00	27.50	-11.50	19°	58.00	98.24	1.76		
415	Apple	1.029 0.484	II	255 1/2	1	1103.5	0	27	103°	103°	168.0	4.0	172.0	60.00	16.00	-13.40	19°	43.71	72.85	27.15		
416		1.029 0.484	II	255 1/2	1	1103.5	17	9	103°	103°	168.0	5.5	173.5	59.65	24.00	-13.75	19°	56.13	94.09	5.91		
417		1.029 0.484	II	255 1/2	1	1103.5	23	4	103°	103°	175.0	6.0	181.0	57.17	23.70	-12.60	18°	53.85	94.20	5.80		
418	Quince	1.024 0.723	III	250 3/4	1	1187.5	0	25	103°	103°	297.0	7.0	304.0	61.70	16.50	-11.55	18°	41.55	67.34	32.66		
419		1.024 0.723	III	250 3/4	1	1187.5	15	6	103°	103°	291.0	18.0	309.0	60.70	25.20	-11.55	18°	54.44	89.68	11.32		
420		1.024 0.723	III	250 3/4	1	1187.5	20	3	103°	103°	290.0	22.0	312.0	60.00	27.00	-11.44	18°	56.94	94.90	5.10		
421	Plum	1.053 1.483	I	260 3/4	1	1187.5	0	20	102°	102°	328.0	21.0	349.0	53.72	13.00	- 9.90	18°	32.59	65.67	39.33		
422		1.053 1.483	I	260 3/4	1	1187.5	10	10	103°	103°	320.0	18.0	338.0	55.47	20.20	- 9.90	18°	44.59	80.38	19.62		
423		1.053 1.483	I	260 3/4	1	1187.5	17	3	103°	103°	329.0	13.0	342.0	54.82	23.60	- 9.30	18°	48.74	88.90	11.10		

Examination of this table emphasizes the general principle previously considered<sup>1</sup>, that the inversion of the sugar depends upon the time of boiling sugar and juice together and also upon the acidity of the latter. In all cases the percentage of sugar inverted increases with the time juice and sugar are boiled together. It should be stated that each of these juices was examined for sucrose, none of which was found, except a trace in red raspberry, and about 0.75 per cent. in currant—so little comparatively that no account was taken of it in the calculations. The absence of sucrose in these juices is probably accounted for by its hydrolysis through the slow cooking of the fruit in extracting the juices and by the boiling in preparation for canning them.

In making these three jelly samples from each fruit, it was expected that some indication, concerning which one of the three might be preferable, would be shown through a difference in texture, color, etc., of the jellies produced, and through some form of sugar finally crystallizing from one or more of the three samples, even though in each case an excess of sugar had been carefully avoided. However, three months after making (the surfaces of the jellies having been carefully paraffined) no trace of crystals of any sort has appeared in any sample. These jellies will be kept for future examination on this point. The jellies of each fruit seemed of uniformly good texture among themselves—the only difference discernible being a slight increase in depth of color depending upon the longer time juice and sugar had been boiled together.

In this connection an interesting economic point appears, on consideration of the columns (Table II) showing weights of skimmings and weights of jelly. In general, the greatest waste of the jelly in the form of skimmings occurs when juice and sugar are boiled together from the beginning. Conversely, the yield of jelly is likely to be greater when the sugar is added near the end of the operation.

The boiling-point at which the jelly-test was observed, and at which the jelly was removed from the fire, was approximately 103° C., with the exception of blueberry, which was found to be slightly lower. This is interesting in connection with the boiling point of cherry and strawberry jellies discussed further on.

*Use of Beet Sugar Compared with Cane Sugar.*—Several experiments were carried out comparing beet sugar and cane sugar in jelly-making. When an equal weight of pure beet sugar was substituted for that of cane sugar to a like volume of juice, the only difference observable was that the volume of jelly produced in the case of beet sugar was slightly less than the volume when cane sugar was used. No difference in the texture or taste of the two jellies was discernible.

*Hydrolysis of Pectin.*—That pectin can be hydrolyzed on sufficiently long boiling in acid solution was shown from the work of Haas and Tollens,<sup>1</sup> who found that pectin heated for eight hours with four per cent. sulphuric acid was hydrolyzed. That the pectin of fruit juices can also be hydrolyzed by the acid present through sufficiently long boiling under a reflux condenser, is probable from the results shown in Table III:

<sup>1</sup> Bureau of Chem., Bull. 66, 52. THIS JOURNAL, 1, 338.<sup>1</sup> Ann. Chem. (Liebig), 286, 278.

TABLE III

No.	Juices.	Sp. gr. of juice	Percent of acid calculated as H <sub>2</sub> SO <sub>4</sub>	Time of boiling, (hours)	Sugar	Result.
1	Current	1.050	3.212	5	3.4	1 No test for pectin
2	Currant	1.048	1.925	10	None	No test for pectin
3	Red raspberry	1.050	1.925	10	3/4	1 No test for pectin
4	Red raspberry	1.050	1.925	10	None	No test for pectin
5	Blueberry	1.055	1.332	16	None	No test for pectin
6	Apple	1.042	0.860	16	None	No test for pectin
7	Plum	1.053	1.483	12	None	No test for pectin
8	Quince	1.024	0.723	18	None	No test for pectin

From these results it would appear that the acidity of the juice modifies the time necessary to destroy the pectin as such (compare 1 and 2). Doubtless the percentage of pectin in the juice modifies the result also—*e. g.*, for blueberry and quince (5 and 8) two juices known to be particularly rich in pectin, a long time was necessary, 16 to 18 hours; though in the case of quince doubtless the low acidity also increased the length of time. Apple juice (6) of moderate acidity comparatively, but of high specific gravity, also required 16 hours. Apparently the presence of sugar in these juices (see 3 and 4, whose acidity is nearly the same) had little or no effect on the time.

From what has been shown, then, it would appear that it is possible to spoil jelly through long heating. In practice this would be unusual on account of the hours of time necessary to hydrolyze the pectin, but a case of this sort did come to the writer's attention through the failure of one home jelly-maker to make her grape jelly "jell." Hours of simmering on the back of the stove had destroyed the pectin.

Further, in the light of these experiments, it may be questioned whether or not it is wise to attempt to use the later juice extractions mentioned earlier in this article, for jellies. It was found, however, that these later extractions could be used for jellies either by first concentrating to a specific gravity approximating that of the first extraction, before determining upon the volume of sugar to be used, or by proportioning the sugar with due regard for the specific gravity and the acidity of the juice. The comparatively short time necessary for concentration, and the low relative acidity (insufficient for hydrolysis under the time condition) did not affect the jelly-making qualities of these later extractions.

The results shown in Table II possibly indicate that sufficiently refined methods for the determination of the percentage of pectin in a fruit juice will reveal the fact that this percentage varies with the condition of the fruit.

*Absence of Pectin from Pine-apple.*—No pectin could be found in cooked pine-apple—the raw juice was unexamined. This lack of pectin in pine-apple explains, of course, the failure to produce jellies from

this juice, which was experimentally demonstrated in the course of these experiments. If the pine-apples in hand, then, were fair samples of their kind, then pine-apple jellies must contain some other juice (apple?) to supply pectin, the jelly-making basis—the pine-apple supplying the flavor.

*Absence of Pectin from Juices of Uncooked Fruits.*—The absence of pectin from the juices of certain uncooked fruits was observed. Little was found in apple, none in quince, lemon, or orange—these being all the raw juices so far examined.<sup>1</sup> As is well known, the juice of cooked apple or of cooked quince each contains an abundance of pectin and these two fruits are among the standards for jelly-making. Of course, it is a simple matter to obtain the raw juices of oranges and of lemons. To obtain the raw juices (cider) of apples or quinces the fruit was cut (pulp with skins and seeds) into quarters, then passed through a meat grinder, and the ground mass drained through cloth. The flavor of these juices was excellent, but no pectin could be detected in the quince juice, and only a small amount in that of the apple. The results of attempts to make jelly from this apple juice led to an opaque, gummy mass, having a strong flavor of apples (see 202 and 203, Table IV). The ground mass above mentioned of either apple or quince, when cooked slowly with water sufficient to cover, yielded a juice containing an abundance of pectin as usual—the quince a superabundance of it. However, such an apple juice refused to make a clear jelly (see 204, Table IV) though the low proportion of sugar ( $\frac{1}{4}$ :1) here used might have had something to do with this, as it certainly did with the tough texture—a low proportion of sugar was here used, however, on account of the low specific gravity (1.020) and the low acidity (0.154) of this juice (most of the acid of the fruit having appeared in the cider, acidity 0.633).

*Extraction of Apple Juice by Use of Double Boiler.*—To avoid any dilution of apple juice the prepared fruit was cooked in a double boiler until soft, then mashed and drained as usual. However, this juice (sp. gr. 1.090 and acidity 0.967) refused to produce a clear jelly even when an equal volume (1:1) of sugar was used (206, Table IV), though the taste was excellent. The remaining pulp, after cooking with water by the usual method, still failed to produce a clear jelly (207, Table IV), though the texture was good.

Nos. 211 and 212, Table IV, show the data of two quince jellies, the second of which was artificially acidified. Such addition of acid (tartaric) improved the texture of this jelly much, and in this instance the taste also:

<sup>1</sup> Since this paper was written, the raw juices of currants and of blackberries have been examined. Each was found to contain pectin, but in less proportion than the juice of the cooked fruit. The jelly made from raw currant juice was not clear. That from blackberry (sugar  $\frac{1}{2}$ :1) was exceedingly clear and of excellent quality.



TABLE IV.

No.	Fruit.	Extraction.	Sp. gr of juice	Per cent of acid calculated as $H_2SO_4$ .	Time of boiling			Texture of jelly.	Remarks.
					Vol. of sugar to juice.	Before adding sugar.	After adding sugar.		
202	Northern Spy apple	Cider	1.057	0.633	3/4 : 1	10	5	Gum	Strong taste of fruit, muddy
203	Northern Spy apple	Cider	1.057	0.633	1/2 : 1	10	20	Gum	Strong taste of fruit, muddy
204	Northern Spy apple	Ext. after cider	1.020	0.154	1 1/4 : 1	40	20	Rather tough	Not clear
205	Northern Spy apple	II	1.027	0.385	1/2 : 1	20	30	Rather tough	Clear, excellent flavor
206	Northern Spy apple	Double boiler	1.090	0.967	1 : 1	..	12	Rather tough	Not clear, flavor excellent
207	Northern Spy apple	Ext. after double boiler	1.0375	0.434	1/2 : 1	20	8	Good	Not clear, flavor excellent
211	Quince	II	1.016	0.589	3/4 : 1	..	..	Soft	
212	Quince	II	1.016	0.877	3/4 : 1	..	..	Good	

*Orange and Lemon Jellies.*—Quite as interesting as the absence of pectin from the raw juices of oranges and lemons is the fact that on cutting either of them into thin slices, adding distilled water and cooking slowly for some hours, an abundance of pectin was found in the resulting drained-out juice. Further experiments located this pectin in the white inner skin. The method of its extraction was as follows: A thin peeling sufficient to remove the yellow, oily portion was cut off, then the thick white skin removed from the pulp. This thick white skin was passed through a fine meat grinder, soaked in distilled water (sufficient to cover) over night, cooked very slowly for several hours, and then drained. This first extraction was particularly rich in pectin. Subsequent extractions of this pulp always showed a considerable proportion of pectin, but decreasing in amount. These extractions, on addition of some of the clear juice from the pulp, for acidity and flavor, yielded excellent jellies. If the thin outer yellow skin had been carefully removed they had little or no bitter taste. The following table comprises some data concerning jellies of oranges and of lemons.

it was acidified either by the raw juice (249, 302) or by some other acid as tartaric (249a).

Then, in what is usually a waste product (the white inner skins of oranges and lemons) we have an abundant source of pectin from which excellent jelly can be made if properly acidified.

*Isolation of a Pure Pectin.*—It was noteworthy that the purest pectin yet prepared in this research was obtained from oranges and lemons. It was isolated by the method heretofore used<sup>1</sup> and was reprecipitated three times. By long manipulation of the precipitated pectin (supported on a very fine cloth suspended from the corners) the liquid was so completely worked out of the substance that a powdery white body, somewhat starch-like in appearance, was obtained. This was dried in a current of dry hydrogen over sulphuric acid.

Ash determinations of orange pectin so obtained showed less than 0.5 per cent. of ash—of lemon pectin about 3.5 per cent. Compare Haas and Tollens. No melting-point of this pectin could be obtained, but the substance, when out of contact with air, chars strongly at 170° C.

TABLE V.

No.	Kind.	Juice extraction.	Sp. gr. of juice.	Per cent of acid calc. as $H_2SO_4$ .	Time of boiling			Results and remarks.
					Vol. of sugar to juice.	Before adding sugar.	After adding sugar.	
239	Orange	Raw juice	1.048	1.932	..	..	..	No pectin, hence no jelly
240	Orange	Cooked whole fruit	1.037	0.482	1/2 : 1	10	10	Thick gum, finally set to fair jelly (bitter, marmalade-like)
242	Orange	Cooked whole skins	1.018	0.123	1/2 : 1	20	20	Thick syrupy gum, bitter
245	Orange	Cooked inner white skin	1.017	trace	1/2 : 1	10	8	Syrup
246	Orange	Cooked outer yellow skin	1.015	trace	1/2 : 1	10	5	Syrup, bitter
247	Orange	Cooked fruit exclusive of yellow skin	1.050	1.031	3/4 : 1	5	8	Good jelly, good flavor
249	Orange	Cooked inner white skin + raw juice	..	1.031	3/4 : 1	5	10	Tender jelly
249a	Orange	Cooked inner white skin + tartaric acid	..	1.031	3/4 : 1	5	10	Good jelly
249b	Orange	Cooked outer yellow skin + tartaric acid	..	1.031	3/4 : 1	5	10	Gum
300	Lemon	Cooked fruit exclusive of yellow skin	1.008	3.988	3/4 : 1	15	10	Firm jelly (sour)
301	Lemon	Cooked inner white skin	1.005	trace	1/2 : 1	15	8	Syrup
302	Lemon	Cooked inner skin + raw juice	1.008	1.039	3/4 : 1	10	5	Excellent jelly

Results given in this table show that if the yellow outer skin is used the product is more or less gummy (240, 242, 246, 249b). Good jellies from the cooked whole fruit, exclusive of the yellow skin, could be obtained (247, 300). The juice from the cooked inner white skin contained a large percentage of pectin, but no jelly (245, 301) could be obtained from it till

It is hoped to continue this work on the isolation and examination of pure pectin.

*Cherry and Strawberry Jellies.*—Although the juices of these fruits contain pectin in abundance and are quite acidic, yet they offer much difficulty if jellies

<sup>1</sup> THIS JOURNAL, 1, 339. Haas and Tollens: *Ann. Chem. (Liebig)*, 286, 278.

from them are attempted. The cause of this difficulty appears to lie in a more or less gummy substance which accompanies the pectin and which interferes with its nice action. An increase of the acidity of the natural acid of the strawberry (by addition of tartaric acid) aided materially in the precipitation of a jelly from this fruit, but the characteristic flavor of the strawberry was destroyed just as in the case of pear and peach jellies. Cherry juice is so strongly acid that further acidification of it was not attempted. (Wild red cherries were found to yield an excellent jelly.)

Experiment finally proved that in making strawberry and cherry jellies reliance could not be placed upon the first indication of the jelly-test as is usual in other jellies, but that the concentration must be continued beyond that point, and the results were best, although not ideal, when the temperature of the boiling mixture was allowed to reach 105° C. No attempt is made at present to account for this—merely the fact is stated. If the concentration was continued beyond this temperature merely a sticky gummy mass resulted. Very interesting in this connection is the statement by Belling,<sup>1</sup> who, in making guava jelly, found that the boiling point must be raised to 113° C. Evidently the temperature is no infallible criterion for determining the jelly point.<sup>2</sup> Of course, to a certain degree undoubtedly, different experimenters would reach different conclusions regarding the point at which jelly is to be considered done, since the personal equation must enter more or less into any decision regarding the texture of jelly which is to be called ideal.

#### SUMMARY.

1. A very frequent cause of failure in jelly-making is the use of too much sugar.
2. The percentage of inversion of sugar most desirable in jellies has not been determined.
3. Beet sugar and cane sugar may be used interchangeably in jelly-making.
4. Pectin of fruit juices may be hydrolyzed by the acids present if boiled sufficiently long.
5. The raw fruit juices, so far examined, contain less pectin than do those of the cooked fruit. Sometimes the former are pectin-free.
6. The white inner skin of oranges and of lemons is a prolific source of pectin.
7. To insure results approximately good, the boiling point of strawberry and of cherry jellies must be allowed to increase (as much as two degrees) above that at which the jelly-test is observed.
8. Owing to variations in specific gravity and acid-

<sup>1</sup> Florida Ag. Exp. Sta. Record, 106, (1908).

<sup>2</sup> The work of Miss Snow (*Farmers' Bull.* 388, 30) regarding the density of jelly at its boiling point may here be cited.

ity of juice, good jellies cannot be made by rule of thumb.

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### THE CHEMICAL AND MINERALOGICAL EXAMINATION OF SOME CHINESE TEA SOILS.<sup>1</sup>

By W. O. ROBINSON AND W. J. MCCAUGHEY.

Received June 3, 1910.

Three samples of Chinese tea soils were submitted to this laboratory for analysis by Dr. Rodney H. True, of the Drug Plant, Poisonous Plant, Physiological and Fermentation Investigations, Laboratory of the Bureau of Plant Industry, U. S. Department of Agriculture. These soils were collected by Vice-Consul H. E. Nightingale, from the northern central part of the Province of Fukien, about 150 miles north of Foochow, at Kienning fu and in the Wu I Shan district.

In this district a tea of very superior quality is grown. The varieties are known as the "Dragons Pool" and "White Coxcomb." These teas are not sold but are given as tribute to the Chinese throne. The growth and picking of the tea is attended with religious ceremony.

The soil is held by the Chinese to be the most important factor in tea cultivation. The object is to produce a rather stunted shrub, for it is held that under these conditions a more desirable flavor is developed in the tea. The culture is very simple, being restricted to digging around the plants twice a year and keeping the weeds pulled. They are seldom, if ever, fertilized.

It is interesting to compare the composition of American soils that have been under cultivation for a comparatively very short time, with these Chinese soils, especially when we consider how very little has been added to these latter by way of fertilizers, and that for thousands of years they have been under a clean cultivation, the tea leaves and weeds having been removed from their place of growth and not returned to the soil. The following analyses represent the compositions of soils that have been under cultivation longer probably than any soils of which we are aware. These soils were weathered from Middle Paleozoic formations. The present altitude is 500-1000 feet. The formation has shown a decided tendency to stand high and probably has been subjected to denudations.

Soil No. 1 came from the Wu I Shan district, which is just south of the Tayuling Mountains.

Soils Nos. 2 and 3 came from Kienning fu, a town on the junction of the Min and Sing ki rivers, about 100 miles above Foochow, in the province of Fukien in South China.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

The following examinations have been made:

1. Chemical, consisting of an analysis for the total constituents and the constituents soluble in hydrochloric acid according to the official method given in Bulletin No. 107 of the Bureau of Chemistry, U. S. Department of Agriculture.
2. Mechanical analysis.
3. Mineralogical examination.
4. An examination made for the purpose of correlating these soils with recognized American types.

The chemical examination shows that the composition is much the same as that of fertile American soils. The phosphoric acid is fairly high, both the total and the acid-soluble. The acid-soluble potash, lime and magnesia are much the same as in the American soils.

The analyses are given in Tables I and II.

TABLE I.—COMPOSITION OF CHINESE TEA SOILS.

Ultimate analysis. Analyses made by W. O. Robinson.

	No. 1 Per cent.	No. 2. Per cent.	No. 3. Per cent.
Loss on ignition.....	10.14	6.69	8.29
SiO <sub>2</sub> .....	54.78	73.97	67.36
FeO.....	9.80	3.65	5.26
Al <sub>2</sub> O <sub>3</sub> .....	22.02	12.48	13.72
TiO <sub>2</sub> .....	0.95	0.53	0.81
MnO.....	0.023	0.014	0.105
CaO.....	0.18	0.28	0.58
MgO.....	0.14	0.32	0.45
Na <sub>2</sub> O.....	0.26	0.34	0.42
K <sub>2</sub> O.....	1.26	1.71	2.32
P <sub>2</sub> O <sub>5</sub> .....	0.51	0.24	0.59

TABLE II.—COMPOSITION OF CHINESE TEA SOILS.

Acid digestion. Official method. Analyses made by W. O. Robinson.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Loss on ignition.....	10.14	6.48	8.01
Insoluble.....	63.98	81.27	79.28
Fe <sub>2</sub> O <sub>3</sub> .....	8.82	3.63	4.41
Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> .....	16.43	7.83	6.63
MnO.....	0.022	0.012	0.095
CaO.....	0.11	0.10	0.23
MgO.....	0.09	0.40	0.41
Na <sub>2</sub> O.....	0.09	0.08	0.09
K <sub>2</sub> O.....	0.39	0.44	0.31
P <sub>2</sub> O <sub>5</sub> .....	0.24	0.14	0.32
Nitrogen by moist combustion.....	0.052	0.068	0.154

The solubility of the potash in these soils is interesting. It will be seen that soil No. 3 is highest in total potash and lowest in acid-soluble potash. By inspection of Table IV it is evident that soil No. 3 differs quite widely in mineralogical composition from No. 1 and No. 2, the most striking difference being the large amount of microcline in No. 3. This

TABLE III.—MECHANICAL ANALYSES OF SOILS FROM CHINA, MADE BY C. C. FLETCHER.

No.	Description.	Organic matter, per cent.	Fine earth				
			Fine gravel, > 1 mm. Per cent.	Fine sand, 1 to .05 mm., P. ct.	Medium sand, .05 to .05 mm., P. ct.	Fine sand, .05 to .01 mm., P. ct.	Very fine sand 0.1 to .05 mm., P. ct.
(1)	Red clay.....	1.8	0	3.4	7.8	4.2	19.4
(2)	Loam.....	5.9	14.3	8.4	12.2	8.4	24.0
(3)	Loam.....	2.4	6.8	6.4	18.1	14.2	30.6

Very fine sand 0.1 to .05 mm., P. ct. Silt, .05 to .005 mm. Clay, .005 to 0.001 mm. Per cent.

mineral is found in the soil with sharp, unweathered faces and is acid-resistant, facts that account for the low solubility of potash.

The mechanical analysis given in Table III shows that soil No. 1 is a heavy clay and that soils Nos. 2 and 3 are loams.

The results of the mineralogical examination are given in Table IV. Examination by W. J. McCaughey:

TABLE IV.

No. 1. Clay soil. The sands are largely quartz; minerals other than quartz relatively low; of these zircon and mica are most abundant. The mica, for the greater part, is biotite. Hornblende, chlorite and tourmaline are present. Hornblende and biotite show weathering and transformation into chlorite.

No. 2. Loam. Minerals other than quartz in the sands are fairly abundant. Micas (biotite and muscovite) very abundant. Orthoclase abundant, being largely kaolinized. Tourmaline is present. Microcline and zircon are common accessories.

No. 3. Loam. Kaolin, quartz, mica (muscovite and phlogopite), microcline, and magnetite are quite abundant. Hematite is present in some quantity, generally as a coating on soil grains. Partly kaolinized orthoclase is a common accessory. Hornblende, epidote, tourmaline and zircon are present. The mica carries inclusions of apatite and magnetite.

It is the opinion of Professor G. P. Merrill, who has kindly looked over the rock fragments in these soils, that Soils Nos. 1 and 2 have probably resulted from the decay of sandstones, the material having been transported but little and being originally derived from granitic material. Soil No. 3 has probably resulted from the decay of a volcanic mud of the trachyte type. The rock fragments contain quartz and are plainly secondary.

There are no soils yet described in the United States that correspond in general type characteristics to these Chinese soils. The nearest approach are the soils of the Cecil, Chester or Durham series. They most resemble the soils in the southern Piedmont plateau and those in Oklahoma, and this fact, in view of the conditions of the climate in these regions, would appear to make these areas desirable for experimental work on tea culture.

BUREAU OF SOILS,  
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## NOTES ON THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

By P. L. HIBBARD  
Received July 29, 1910.

The routine chemist usually follows some official or prescribed method, with little thought as to the reasons for each step, or the effect of variations. He should know the effect of varying time, temperature, quantity of reagents, and size of apparatus on his results. In view of these needs the following experiments were made. It is to be understood that they cover only part of the ground and that only a few of the possible variations have been tried. Naturally the practice in different laboratories varies to some extent.

*Conditions of the Experiments.*—Substance taken —1.401 grams (ground to pass 1 mm. sieve) with



25 cc. sulfuric acid and 10–12 grams of a mixture of potassium sulfate with 5 per cent. of copper sulfate. The substance to be analyzed is placed in a 500 cc. round-bottomed Jena flask, neck about 6 inches long, 1 inch diameter. The potassium sulfate mixture is added and mixed with the substance to avoid balling, then the acid is added and mixed and the flask supported at an angle of  $45^\circ$  on an asbestos ring 2 inches in diameter of opening. It is heated by a Bunsen flame, regulated so that the acid boils gently, and volatilizes slowly. During three hours' digestion it may lose one-third the volume of acid. After the digestion it is cooled, 250 cc. are water added, a little granulated pumice and enough strong caustic soda, 50–60 cc., to make alkaline. After connecting with the condenser, the flask is shaken to mix the contents. It is then heated by direct flame so that about 200 cc. are distilled off in course of about one hour. The ammonia is collected in standard half normal hydrochloric acid, the excess of which is titrated back with standard tenth-normal ammonia with cochineal indicator. Thus, the result is found as percentage of nitrogen without tables or calculations.

1. *Time for Digesting Dried Blood.*—Used an ordinary sample, which contained, as an average of five determinations by regular method, 13.27 per cent. nitrogen.

Time digested. Hour.	Per cent. nitrogen found.
3	12.80
1	13.00
1½	13.10
2	13.22
3	13.27
5	13.27

Three hours seem to be sufficient time.

2. *Time for Digesting Bone Meal.*—Used a sample of steamed bone, rather high in nitrogen.

Time digested. Hour.	Per cent. nitrogen found.
3	3.87
3½	3.88
1	3.93
1½	3.98
2	3.99
3	4.04, 4.05 Two determinations
4	4.05
5	4.04, 4.05 Two determinations

Time needed, about three hours.

3. *Time for Digesting Nitrate of Soda to Reduce it to Ammonia by Ulsoh-Street Method.*—Used same flasks as for Kjeldahl work, in which were placed 25 cc. of a solution containing 0.5 gram of sodium nitrate, added 5 grams iron powder (reduced by hydrogen), and 20 cc. of 1 : 3 sulfuric acid. After standing for varying time, added 50 cc. water, heated to boiling for 30 minutes. Cooled, added 200 cc. water, 30 cc. caustic soda, and some pumice, distilled as in Kjeldahl method.

Time digested before heating. Hour.	Per cent of nitrogen.
0	15.44
¼	15.55
½	15.53
1	15.53
2	15.53
4	15.47
6	15.36

It appears that very little time is required for digestion before heating. On account of the long time in the two last experiments all the acid was used up by the excess of iron present so that on boiling 30 minutes some basic iron sulfate was formed and some ammonia thereby expelled. Hence, it is concluded that an excess of acid should be used, at least 25 cc. 1 : 3, and thus prevent loss of ammonia.

4. *Time Required to Expel Ammonia in Distillation of Kjeldahl Digestion.*—One gram ammonium sulfate placed in flask same as for regular Kjeldahl distillation. Added water and soda, etc., distilled as usual. Some cochineal was placed in the receiver and tenth-normal hydrochloric acid added gradually as was needed to neutralize the ammonia distilled over.

Time Min.	Volume distilled	cc. N/10 HCl used.
2	...	42
4	...	85
6	...	122
8	...	137
10	51	145
14	...	148.5
19	100	149.0
24	...	149.0
29	160	149.0
45	220	149.0

Thus shown that 15 minutes' boiling will expel nearly all the ammonia, which comes over with about 75 cc. of water. The amount of ammonia present at the start was as much as is found in the ordinary Kjeldahl determination.

5. *Time Required to Expel Ammonia by Distilling with Magnesium Oxide.*—Experiment conducted like the preceding, but using 5 grams MgO instead of the soda solution and having present 0.5 gram ammonium sulfate. On account of the greater tendency to foam, the distillation with magnesia must go slower than with soda, yet this experiment shows no great difference between the two. A parallel experiment with soda was made following this, and the results are presented together.

Time. Min.	MgO.		NaOH.	
	Volume distilled cc.	N 10 HCl used. cc.	Volume distilled. cc.	N/10 HCl used. cc.
2	...	30	...	34
4	...	40	...	84
6	...	58	...	63.5
8	...	61	...	68.5
13	31	69	34	71.5
12	...	72	...	73.3
17	...	73.8	59	74.5
23	...	74.4	...	74.7
27	96	74.5	...	74.7
42	146	74.5	155	74.7
52	196	74.5	...	...

Thus shown that it is not necessary to distil nearly to dryness with  $MgO$  to obtain all the ammonia.

6. *Optimum  $K_2SO_4$  for Kjeldahl Digestion.* Same Apparatus as for Experiment 1.—1.401 grams dried blood, 25 cc.  $H_2SO_4$  and varying amount of  $K_2SO_4$ .

$K_2SO_4$ Grams.	Time till clear.	Time digested.	Color of diluted solution.	Per cent. nitrogen.
2.....	did not clear	6 hours	Yellow	12.98
4.....	3 hours	3 "	Yellow	12.95
6.....	2 1/2 "	3 "	Yellowish	13.00
8.....	2 "	3 "	Colorless	13.15
10.....	1 3/4 "	3 "	"	13.33
12.....	1 1/2 "	3 "	"	13.32
14.....	1 1/4 "	3 "	"	13.40
16.....	1 "	3 "	"	13.41

On account of difficulty during distillation, it seems not desirable to use more than 10–12 grams  $K_2SO_4$  and this is not sufficient to secure complete oxidation within three hours, so copper sulfate is added, hence the following experiments with  $CuSO_4$ .

7. *Optimum  $CuSO_4$  for Kjeldahl Digestion.*—Similar to last experiment using 10 grams  $K_2SO_4$  in each test, but varying  $CuSO_4$ .

$CuSO_4$ Grams.	Time till clear. Min.	Total time heated Hours.	Per cent. nitrogen.
0 .....	70	2	13.10
0.2.....	45	2	13.35
0.4.....	38	2	13.37
0.6.....	35	2	13.38
0.8.....	30	2	13.34
1.0.....	30	2	13.34
1.5.....	30	2	13.34
2.0.....	30	2	13.27

In order that the effect of the different amounts might be more easily seen the digestion was continued for only 2 hours, which was not long enough to obtain all the nitrogen.

#### ANOTHER SET.

$CuSO_4$ .	Time till clear. Min.	Total time heated. Hours.	Per cent. nitrogen.
0.5.....	35	3	13.50
0.5.....	35	3	13.47
1.0.....	35	3	13.36
1.0.....	35	3	13.27
2.0.....	35	3	13.27
2.0.....	35	3	13.23

With 0.5 gram  $CuSO_4$  and 10 grams  $K_2SO_4$ , and heating three hours, the results were pretty nearly correct. Cause of low results with upward of 0.5 gram  $CuSO_4$  is unknown. However, more than 1 gram is useless, as it is simply dehydrated and remains undissolved in the acid. The equal time required to become clear, with varying amounts of  $CuSO_4$ , indicates that the larger amounts do not hasten oxidation.

It seems desirable to use not much more than half a gram of  $CuSO_4$ . The third set was run with 0.5 gram  $CuSO_4$  and varying  $K_2SO_4$ .

$K_2SO_4$ Grams.	Time till clear Min.	Total time heated. Hours.	Per cent. nitrogen.
2 .....	120	3	13.12
4 .....	65	3	13.28
6 .....	45	3	13.43
8 .....	40	3	13.45

Results not high enough.

Using 0.8 gram  $CuSO_4$ .

6.....	55	3	13.48
8.....	36	3	13.54
10.....	32	3	13.56
12.....	28	3	13.54

The larger quantity of copper seems able to replace some of the  $K_2SO_4$ . From all of these results it seems that 10 grams  $K_2SO_4$  with 0.5 gram  $CuSO_4$  is the most suitable combination. Using this mixture the following results were obtained:

Heated 3 hours.....	13.53, 13.52 per cent. nitrogen.
Heated 6 hours.....	13.48, 13.53 per cent. nitrogen.
Heated 10 hours.....	13.55, 13.56 per cent. nitrogen.

Three hours' heating seems sufficient.

8. *Prevention of Bumping.*—In this connection, it is interesting to note that presence of the excess of  $CuSO_4$  which remains insoluble in the boiling acid prevents the bumping which often accompanies this method of digestion, but as it tends to cause low results,  $CuSO_4$  cannot be used.  $FeSO_4$  crystals were tried and found to prevent bumping as well as  $CuSO_4$ , but without causing low results for nitrogen. Probably  $Fe_2(SO_4)_3$  would be better, but not being at hand it was not tried. In case a digestion bumps badly, a gram or two of crystallized ferrous sulfate dropped; it nearly always produces quiet boiling.

9. *Loss of Ammonia during Digestion, through Dissociation of Ammonium Sulfate.*—It has been said that in the Gunning nitrogen determination there is danger of loss of ammonia, if the flame strikes the flask above the level of the acid, thereby dissociating  $(NH_4)_2SO_4$  with loss of  $NH_3$  due to high temperature. In order to settle this question several experiments were made.

(1) One gram  $(NH_4)_2SO_4$  plus 25 cc.  $H_2SO_4$  in 300 cc. flask connected with condenser. Distilled off two-thirds of the acid. The distillate was neutralized and distilled; only a trace of  $NH_3$  found in it. Flask heated with bare flame.

(2) Similar to (1) but added 10 grams  $K_2SO_4$   $CuSO_4$  mixture as for regular nitrogen determination. Distilled off two-thirds of the acid with bare flame. Found in distillate nitrogen = 0.020 gram = 2 per cent. on ordinary determination. Presence of  $K_2SO_4$  seems to cause loss of nitrogen along with the acid distilled over.

(3) Used same materials as in last experiment but placed in regular 500 cc. flask and heated as for regular nitrogen determination. The vapors coming from the mouth of the flask were collected, neutralized, and distilled for  $NH_3$ . For the first two hours' heating the distillate contained only a trace of  $NH_3$ . For the

third hour, found in distillate  $\text{NH}_3 = 0.015$  gram  $\text{N} = 1.5$  per cent. Stopped heating as most of the acid was distilled out.

(4) Used a sample of dried blood, run as for regular nitrogen determination, except heating faster and collecting acid and other vapors distilled out. First hour, found in distillate  $\text{NH}_3 = 0$ , during this time about half the acid was distilled out. After 15 minutes more, stopped heating as nearly all free acid was expelled. Found in second distillate  $\text{N} = 0.008$  gram; in digestion flask  $\text{N} = 0.051$ . Out of 13.5 per cent. present at start only 5.9 per cent. were recovered. The other 7.6 per cent. were lost through dissociation or some other cause, unknown. These extreme and unusual conditions proved the possibility of loss. It was next determined that under ordinary conditions there is no loss.

(5) Same as last experiment but heated 3 hours supported by large asbestos rings as in usual manner for nitrogen, determination, except that the rings were large enough so that a portion of the flask was exposed to the flame above the level of the acid. Lost about 20 per cent. of total acid. Found in the digestion, two tests 13.52, 13.53 per cent. nitrogen.

(6) Like the last but heated 6 hours on small rings, boiled gently. Nearly half the acid was lost; found, two tests,  $\text{N} = 13.48$ , 13.53, hence no loss occurred.

(7) Similar to last, but used large asbestos rings; heated at ordinary rate. After 3 hours' heating added 10 cc. more acid, after next two hours' heating added 10 cc. acid again. Continued heating 5 hours longer. Total time heated 10 hours. Total acid used 45 cc. Acid remaining in flasks, about 30 cc. Found  $\text{N} = 13.55$ , 13.56 per cent.

From this it is concluded that if the volume of acid does not fall below 20 cc. there is no danger of loss of nitrogen even though the flame strikes the naked flask above the acid.

#### SUMMARY.

(1 and 2) About three hours are required to obtain all the nitrogen in dried blood or bone meal by sulfuric acid digestion with 10 grams  $\text{K}_2\text{SO}_4$  plus 0.5 gram  $\text{CuSO}_4$ .

(3) Using the Ulsch-Street method, only a few minutes are required to change the nitrogen of nitrates to ammonia.

(4 and 5) In distilling ammonium salts with soda or with magnesia, nearly all the ammonia, together with 50-75 cc. water, is obtained during the first 10-15 minutes.

(6) About 10 grams  $\text{K}_2\text{SO}_4$  is the most satisfactory quantity for aiding the acid digestion of nitrogenous substances.

(7) One-half gram  $\text{CuSO}_4$  added with the  $\text{K}_2\text{SO}_4$  hastens oxidation about as well as larger amounts. Much more than this seems to cause loss of nitrogen; the reason for such loss is not known.

(8) Bumping of the digestion is prevented by addition of 1-2 grams ferrous sulfate.

(9) Loss of ammonia during the acid digestion occurs when a large portion of the acid has been driven out by too much or too long continued heat; but not because the flask is heated by the bare flame above the level of the boiling acid. Or, it may be said that loss occurs when, owing to loss of acid, the boiling point of the residue rises too high.

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## ADDRESSES.

### THE ELECTROLYTIC PREPARATION OF CALCIUM.<sup>1</sup>

BY ARDIN R. JOHNSON

It is the main purpose of this paper to set forth the most essential results of considerable experimental work upon the electrolytic preparation of metallic calcium, carried out in the electrochemical laboratories of the University of Wisconsin during the school year 1905-1906. The work was written up and presented as a thesis toward the baccalaureate degree in engineering, but was never published in a scientific journal.

Several good papers have been published in the last three or four years on the preparation of calcium, some by members of this society. It is therefore my object to present only data and statements that will largely supplement or reinforce much that has already appeared in print in leading journals.

While the thesis as originally written up four years ago contains an historical review of experimental endeavors in this line, I shall forego the presentation of the same here for the reason that the work has already been well given by Mr. F. C. Frary.<sup>2</sup> But my observations and data obtained upon two or three typical styles of apparatus much used—apparatus with typically inherent faults, and also an electrolyte with all the common capricious properties, will, I think, be of some value to the many electrochemists who, of late, have become interested in the chemical and metallurgical properties of this element.

The main efforts to produce calcium seem to have been through the medium of a correctly designed apparatus for electrolyzing, and if we glance over the different designs we shall recognize just two different types: First, the apparatus of the Borchers type for utilizing an extremely high current density and consequently obtaining the calcium in a molten condition, in which it rises to the surface and is skimmed off, and secondly, the Rathenau type, which requires that the calcium come out in a compact form, that is, plated out at a moderately low current density.

*Experiments with Apparatus No. 1.*—In view of the successful results which have been attained by the above mentioned experiments, using the Rathenau type of apparatus, I decided also to begin the study of the electrolysis of  $\text{CaCl}_2$  with an apparatus of this class. Accordingly the design shown in Plate II was followed, making use of such data concerning dimensions of anode and cathode as could be gleaned from the published description of Goodwin and Woehler's apparatus.

While a goodly number of trials with this apparatus were carried out, most of which were not over two to three hours duration, only three or four performed under different conditions will be described.

A run was made using pure  $\text{CaCl}_2$  of the very best grade, made by Baker & Adamson. The cylindrical, graphite vessel was filled with  $\text{CaCl}_2$ , and then by the use of the auxiliary elec-

<sup>1</sup> Read before the Chicago meeting of the American Electrochemical Society, October 13-15, 1910.

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **16**, 185 (1909)



trode an arc was struck with the inner surface of the anode container, and the  $\text{CaCl}_2$  gradually melted down in the vicinity of the arc until a small pool of fused  $\text{CaCl}_2$  was formed. The

under the influence of the convection currents. It was immediately recognized that a furnace of the Borchers type was at hand, so the current was gradually cut down as low as 40 to 50 amperes (10 volts drop across cell), at which point a reguline deposit was noticed forming at the end of the rod. But it was now found impossible to keep all the bath fused next to the anode, and finally there was only a comparatively narrow channel of molten salt between anode and cathode. A glowing phenomenon, like a sheet of small arcs, was noticed at the anode. After the bath had been in operation under these conditions some time the iron rod was raised a trifle and electrolysis continued. The calcium "rod" which was forming was very irregular in cross-section, and continued in spite of all efforts to "neck down" until the "rod" suddenly melted, causing an arc and interrupting electrolysis. Part of the calcium formed was skimmed out before the bath solidified and the remainder gotten afterwards by loosening the solid  $\text{CaCl}_2$  from the walls of the anode vessel by immersion in  $\text{H}_2\text{O}$  and then breaking the solid chunk to pieces.

It was also noticed in this bath, as well as in all others, that the current had passed through the bath comparatively near the surface and hence the bath was melted to only a shallow depth, while at the bottom of the anode-containing vessel the bath had remained solidified and almost pure white, though the upper portion through which the current had passed for a long time during electrolysis was very dark colored.

Woehler used a mixture of 100 parts of  $\text{CaCl}_2$  and 17 parts of  $\text{CaF}_2$  by weight for his bath, thus getting an electrolyte which

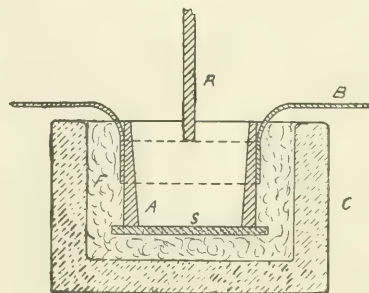
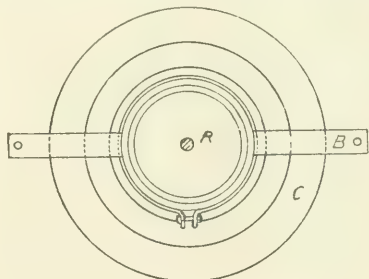


Plate II.

Electrolyzing Apparatus No. 1.

- A—Circular graphite anode.
- B—Metallic conductor connecting with bands on anode vessel.
- C—Soapstone bottom for anode.
- C—Portland cement vessel.
- F—Space filled with asbestos-cement.
- R—Iron and cathode (fastened to a stationary upright screw).

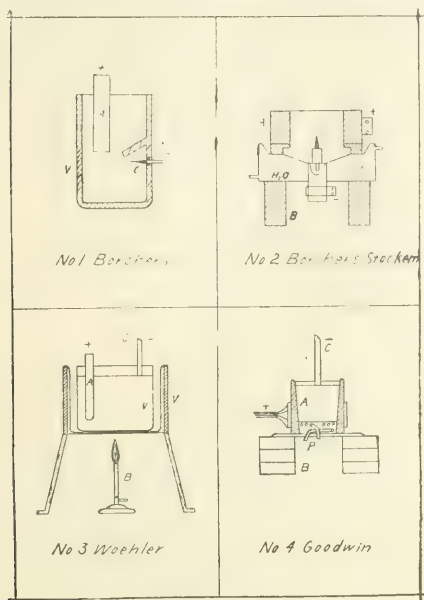


Plate I.

No. 1. Borchers Apparatus.

- V—Iron container for electrolyte.
- A—Carbon anode.
- C—Iron needle cathode insulated from container.
- S—Shelf under which molten calcium may collect.

No. 2. Borchers-Stockem Apparatus.

- A—Circular graphite anode.
- C—Iron needle cathode.
- H—Water-cooled bottom insulated from anode.
- B—Brick support.

No. 3. Woehler Apparatus.

- A—Graphite anode.
- C—Iron cathode.
- V—Iron electrolyzing vessel.
- V—Sheet-iron jacket.
- B—Bunsen burner for melting bath.

No. 4. Goodwin Apparatus.

- A—Graphite, circular anode container.
- C—Iron cathode (fastened to stationary upright screw).
- F—Water pipes for keeping bottom of vessel cool.
- B—Brick support.

auxiliary electrode was now inserted directly into the fused  $\text{CaCl}_2$  and the current caused to flow through the bath directly. When sufficient electrolyte was melted the iron cathode  $R$  was lowered into the molten mass by means of the screw ( $R'$ ) and electrolysis begun. After a period of three or four minutes at most the odor of chlorine was noticed, and there was considerable cracking and snapping at the cathode and bursting forth of yellow flames. The current was gradually increased until finally the whole bath was in a state of fusion and 90 to 100 amperes were flowing. After waiting some minutes the iron cathode was cautiously raised from the bath, but nothing was observed until an arc was struck between the end of the rod and the surface of the bath. The rod was again lowered and electrolysis continued for 15 to 20 minutes, at the end of which time bright beads of metallic calcium were noticed to coalesce around the iron rod and finally break away and swim around in the bath

fused at a much lower temperature. Hence several trials were carried out in the apparatus described, using such an electrolyte. The  $\text{CaCl}_2$  was from the same bottle as that used in the previous trials while the  $\text{CaF}_2$  was ordinary powdered fluorspar.

The two salts were intimately mixed together and then fused down as previously described. After adjusting the current to 40 to 50 amperes it was noticed that a larger portion of the bath was kept in a fluid condition than when  $\text{CaCl}_2$  only was used as electrolyte. Again the melt seemed to be more liquid. Calcium was noticed to form quite rapidly at the cathode but not in a good, compact form. It grew out from the end of the iron rod in a very irregular manner, tending to extend across the anode and short-circuit the bath. Difficulty was experienced in getting a piece even an inch long on the iron cathode, an arc always being struck and melting off all the calcium.

While no attempt will be made to discuss here the chemical phenomena of the baths tried, it may be well to point out the mechanical defects of the apparatus as viewed from an engineering standpoint:

1. The parts of the apparatus (anode container and cathode) are wrongly proportioned to obtain proper cathode current density and still keep the electrolyte in a proper state of fusion.
2. The space intervening between anode and cathode is too small, allowing short circuits to occur.
3. The upper portion of the graphite anode vessel exposed to the air rapidly disintegrates, allowing carbon to fall into the bath.
4. When the bath solidifies the graphite anode container is cracked to pieces.
5. The metallic bands around the anode vessel become badly corroded, causing poor contact.

*Experiments with Apparatus No. II.*—In order to obviate some of the objections to the foregoing apparatus and at the same time have an apparatus practically the same capacity as Goodwin's, I designed that shown in Plate III.

My chief aims in the design of this apparatus were as follows:

1. To have an anode vessel with the same internal dimension as Goodwin's apparatus.
2. An anode container which would not be cracked to pieces when the bath solidified and could be subjected to heavy currents and hard usage.
3. Large enough space between anode and cathode so that iron rods of various cross-sections could be tried as cathode.
4. An apparatus which would have as little radiating surface as possible.
5. To have the exposed portions of the graphite container protected from the atmosphere.

In almost all the trials with this apparatus the  $\text{CaCl}_2$  and  $\text{CaF}_2$  were in the proportions of 100 to 17, respectively. Some of the experiments were carried out with the pure so-called anhydrous  $\text{CaCl}_2$  which has hitherto been described, while others were performed using crystalline  $\text{CaCl}_2$  which was first dehydrated. I shall first describe a run for calcium using the pure "anhydrous"  $\text{CaCl}_2$ .

A granulated carbon resistance furnace was first constructed and a weighed amount of  $\text{CaCl}_2$  placed in a Battersea clay crucible which sat in the carbon resistor. As the  $\text{CaCl}_2$  warmed up, some steam came off and then a very little  $\text{HCl}$ . The whole mass then came to a state of quiet fusion at a very light cherry-red color. Approximately the requisite amount of  $\text{CaF}_2$  was now slowly added and its action in the bath observed. The  $\text{CaF}_2$  seemed to gradually and easily dissolve in the bath. At the same time the bath as a whole grew more and more fluid and limpid. When all of the  $\text{CaF}_2$  had been added the bath seemed to have a cloudy appearance, some portions being rather transparent, while light yellow clouds floated about in other portions. After agitation and maintenance of bath in fused condition for some time it became fairly homogeneous and opaque in appearance.

From the Battersea crucible the fused mass was poured into the electrolyzing apparatus. An alternating current was now passed through the bath, using a carbon rod an inch in diameter as the second electrode. A sufficient current to keep the electrolyte in a well fused condition was found to be about 200 amperes.

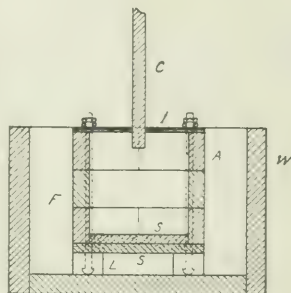
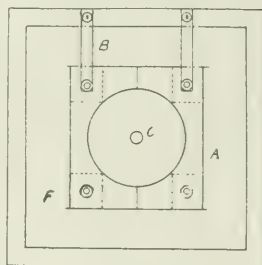


Plate III.

*Electrolyzing Apparatus, No. 2.*

- A—Graphite anode built up of six sections, and held together by bolts in corners.  
 W—Wooden case.  
 F—Intermediate space packed with asbestos cement.  
 S—Loose soapstone bottom.  
 S'—Soapstone bottom bolted fast to anode.  
 L—Carbon legs.  
 C—Iron cathode (fastened to stationary upright screw).  
 B—Copper conductors leading to iron covering, I, which is held down on the top of anode by the corner bolts.

At the surface of contact of the large electrode with electrolyte all was quiet excepting perhaps now and then a faint glow. The small electrode, however, was completely enshrouded with first a glowing sheet of flames and outside of this a circle of yellow flames bursting from the surface of the bath. In the space intervening, only now and then appeared a small yellow flame.

The alternating current was now switched off and the direct current switched on after first replacing the small electrode with an iron one 1 centimeter ( $3/8$  inch) in diameter. Chlorine was immediately detected coming off, and after some time calcium was noticed at the cathode, but it was soon in a molten condition and had to be skimmed from the bath. The current was gradually cut down to 75 or 80 amperes before calcium would adhere to the end of the rod in a reguline condition. With this current, however, only about  $1/4$  to  $1/3$  of the bath was fused. A sort of irregular mass of metallic calcium plus adhering  $\text{CaCl}_2$  was built out from the end of the rod, after an hour's run.

The presence of water in the  $\text{CaCl}_2$  has an important influence upon the results attained, and in view of this fact several runs were tried, using  $\text{CaCl}_2$  which had been subjected to dehydration as follows:  $\text{CaCl}_2$  loaded down with water of crystallization

was placed in the Battersea crucible of the electric resistance furnace above described, and gradually "boiled down." When the mass had reached a pasty condition, a considerable volume of HCl came off, and then it soon began to melt down into a cherry-red, pasty fluid. Small bubbles of gas were noticed rising to the surface, exploding with a loud report and bursting in a yellowish flame sometimes tinged with a bluish color.

All of the electrolyte was next poured into the electrolyzing apparatus and subjected to a high temperature by passing an

ing on research work, it is first, desirable to give some facts concerning the physical nature of the deposit of calcium and the manner in which it forms in reguline condition.

Of course it will be assumed that the electrolyte is in good working condition chemically and otherwise, all conditions being such as to contribute to the best formation of metallic calcium. My experiments have shown that whether the metal comes out with a coarse crystalline structure (as it usually does), or in a compact, dense form, the deposit cannot form to any great thickness before becoming nodular on the surface, or even growing out in arborescent forms.

From analogy with the nature of deposits from aqueous solution (and also because of the particular design of apparatus used), the above results might be anticipated. In the refining of metals from aqueous solutions by electrolysis it has been found practically impossible to obtain a smooth deposit deeper than 4 cm. (1.5 inches), and in most cases the deposit becomes very nodular and uneven by the time the deposit is 1.25 cm. (1/2 inch) thick.

There is no reason to believe that a reguline deposit from  $\text{CaCl}_2$ , or any other fused electrolyte should come out in a smooth compact form for a practically indefinite thickness than there is in an aqueous solution. A glance at a calcium deposit which has been sawed through will show that these formations have a core of fairly solid metallic calcium. This core is particularly solid near the base of the iron rod, but as we leave the center of this core and approach the outside of the formation we find the metal becoming more and more irregular and mixed mechanically with more or less  $\text{CaCl}_2$ . Still farther from the center of the core the metallic calcium and  $\text{CaCl}_2$  are hopelessly mixed together. (This fact has an important bearing upon the values obtained for current efficiency, as will be shown later.) To be sure, an irregular cathode deposit of considerable length can be formed but there is a greater waste of calcium and  $\text{CaCl}_2$  and hence lower and lower efficiency as the "rod" grows longer, on account of the increased mixing of the electrolyte with the metallic calcium formed. It must be borne in mind that a piece of this deposit, consisting of metallic calcium and  $\text{CaCl}_2$ , so intimately mixed mechanically as to appear almost homogeneous, can still be a very good conductor of the electric current and hence may act as a cathode surface for a further deposit of metallic calcium, or a mixture as described, so that a stick of "metallic calcium" such as this is easily obtained.

Again, as intimated above, the particular design of electrolyzing apparatus used is such as to cause the formation of a more or less irregular calcium deposit. When we pass an electric current through this apparatus the current will seek that path which offers the least resistance, and of course we find the lines of current flow as near the surface of the electrolyte as possible. Indeed, as a consequence, the bath remains comparatively shallow in spite of a considerable increase of current. We cannot put the end of an iron rod into the electrolyte to act as cathode without exposing a small portion of the side of the rod, as well as the bottom, to the electrolyte. Consequently more current will enter the edge, or side, of the rod, and hence a tendency for more calcium to deposit around the edge of the rod than directly on the flat end.

Cathode current density has been found to have an important effect upon the structure and nature of the deposit and hence upon current efficiency also. As it is a great objection to this "calcium rod" idea that nothing definite concerning the effects of current density can be determined, because, as the deposit grows the actual cathode surface is continually changing. However, since the current density is continually changing, the conditions under which a reguline deposit is formed are continually changing.

In regard to the use of iron rods of different diameters as

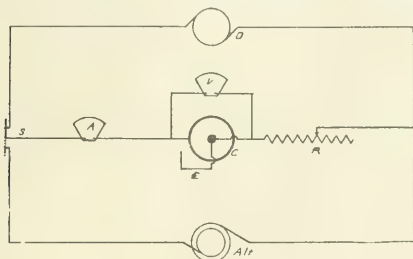


Plate IV.

Showing Connections for Apparatus Nos. 2 and 3.

C—Electrolyzing vessel

E—Auxiliary electrode.

V—Voltmeter.

A—Ammeter.

S—Switch.

R—Rheostat.

D—Direct current dynamo.

Alt.—Alternator.

alternating current of about 200 amperes. A profusion of yellow flames was noticed bursting forth from around the small electrode and the whole surface of the electrolyte became covered with large transparent bubbles, up to 2.5 cm. (1 inch) in radius, of gas (hydrogen) which burst into highly colored flames with a loud report. If the heating be continued these transparent bubbles almost entirely disappear after a time, but no matter how long we continue to heat the electrolyte (or electrolyze) we never get rid of the small yellow flames around the smaller electrode (cathode, if electrolyzing).

Now there are two conditions under which we may electrolyze the above mentioned electrolyte: (a) Electrolyze after all of the gas bubbles (excepting those giving yellow flames) disappear; or (b) electrolyze before the formation of bubbles ceases.

In the first case chlorine is noticed coming off immediately after switching on the direct current. Metallic calcium also appears at the cathode and comes out regularly, if proper conditions of temperature and current are maintained.

On the other hand, if we attempt to electrolyze before the  $\text{CaCl}_2$  is as thoroughly "dehydrated" as possible, that is, before the cessation of gas formation, we get entirely different results. If the bath has been heated little previously, we get almost no chlorine given off at the anode, while at the cathode nothing is deposited if the temperature and cathode current density are high, and if within proper limits, a black, crispy mass, resembling charcoal in appearance, and having seemingly good electrical conductivity, is formed. By long continued electrolysis one may succeed in finally getting a poor reguline deposit, but the bath acts very capriciously at all times.

In a preceding paragraph was set forth the chief aims in the design of apparatus No. 2, with which the above experiments were performed. These experiments have shown the apparatus to fulfil most of the requirements, but before proceeding with the chief objections to this general type of apparatus (Rathenau principle) for use either as a commercial apparatus or for carry-



starting cathodes, it may be stated that with the apparatus in hand it was found that if a rod much less than 1 cm. ( $3/8$  inch) in diameter was used the current density and hence the heating effect was so great that calcium would not form in the solid condition, while if a much larger rod were used the deposit was very crystalline and irregular and mixed with  $\text{CaCl}_2$  even near the base of the iron rod.

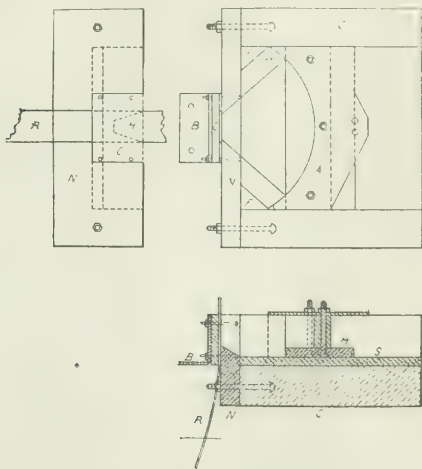


Plate V.

*Electrolyzing Apparatus No. 1.*

C—Portland cement casing.

N—Soapstone end.

S—Soapstone bottom.

W—Soapstone sides.

M—Soapstone base for anode.

A—Graphite anode.

H—Aperture in soapstone end N.

R—Iron ribbon as cathode, to slide between soapstone end N and iron block C.

B—Copper conductor fastened to iron block C.

Connections for apparatus same as for apparatus No. 2.

*Experiments with Apparatus No. III.*—Before taking up the question of current efficiency and in view of the inherent faults in the design of the apparatus used up to this time, I shall describe an electrolyzing apparatus of my own design in which I have endeavored to overcome some of the difficulties.

In the design of this apparatus I have endeavored to attain the following:

1. An apparatus in which the anode and cathode surfaces shall be definite under all conditions.
2. To be able to vary the current density and note the effects upon the electrolysis.
3. To accomplish the removal of the deposit of calcium as fast as formed without interfering with the uniformity of conditions.
4. Construction such that it would stand many "runs."
5. To confine the current to a definite amount of electrolyte, and to an invariable course through the same.

As in the preceding experiments, 100 parts of  $\text{CaCl}_2$  and 17 parts  $\text{CaF}_2$  were fused down in a Battersea crucible by means of a resistance furnace and after being thoroughly mixed were poured into the apparatus. Here, after first being thoroughly heated for some time with an alternating current (a carbon block was attached to the ribbon cathode in the opening H), the direct current was switched on and electrolysis started. As

the metallic calcium deposited to a sufficient thickness the iron ribbon was gradually raised, presenting new cathode surface.

Paul Woehler states that in his experience electrolyzing  $\text{CaCl}_2$  and  $\text{CaF}_2$  by the Rathenau method that a cathode current density of from 45 to 250 amperes per square centimeter can be used and a stick of calcium obtained. He based his figures upon the fact that the amount of current flowing through his apparatus was constant, but the cross-section of the calcium stick varied at different parts. This is obviously a wrong basis upon which to come to such a conclusion, however. Nevertheless, my apparatus at first constructed had a cathode surface of such size that when sufficient current flowed to cause the whole bath to be in a well fused condition, there was a density of 45 to 50 amperes per square centimeter. The first two trials, however, proved that even this cathode current density is altogether too high, for the calcium would not deposit on the iron ribbon, but simply melted and floated about in the bath.

The cathode opening (A) was then made larger and other runs made. A run made when the electrolyte was in good condition showed that calcium came out in the best physical condition at about 10 amperes per square centimeter. To be sure, calcium will come out at a considerable higher current density, but under the particular set of conditions under which these experiments were performed the above current density was found to give the best results. At a lower current density the calcium carries up more  $\text{CaCl}_2$  with it, which tends to solidify just above the surface of the bath and cause the iron ribbon to be cemented fast.

If the calcium does not sufficiently alloy with the iron (which seldom happens), the two will break apart upon cooling some distance above the bath on account of difference in rate of contraction of the two metals. When the calcium does alloy with the iron ribbon, the latter expands at these places, giving rise to little "hills" in the ribbon. Examination of the iron at these points after removal of the calcium shows it to be softer and rotten.

Anode current density is not of so great importance as is cathode current density. We simply need sufficient anode surface over which the  $\text{CaCl}_2$  bath can fuse as far as it likes with the given current in use. If the anode density is unduly great, arcing or glowing phenomena take place at the junction of the carbon and fused bath increasing the total resistance offered by the cell.

*Current Efficiency.*—While the current efficiency at which calcium can be reduced from its chloride is of great importance from an engineering standpoint, yet if the exact conditions under which efficiency is obtained can be maintained are not known, the figures have lost much of their value. Still, although we do not understand fully the nature of the process, to know what efficiency can be attained at times is interesting and encouraging.

Both Goodwin and Woehler made current efficiency determinations, and not only their results, but also their methods of determining them were very different. Goodwin determined the current efficiency for a run of several hours duration, using only  $\text{CaCl}_2$  as electrolyte. He separated the metallic calcium from the  $\text{CaCl}_2$  by pounding loose the encasing  $\text{CaCl}_2$  which had solidified about the "rod" of calcium. The calcium thus mechanically separated was weighed and the efficiency figured. His highest efficiency was 40 per cent.

On the other hand, Woehler, who electrolyzed 100 parts of  $\text{CaCl}_2$  and 17 parts of  $\text{CaF}_2$ , made a mark on the forming calcium rod at the level of the bath, electrolyzed five minutes (gradually raising the rod) and made another mark at the level of the bath. This section was cut out after the run and dissolved in a weak acid solution, the hydrogen collected, and from this the amount of calcium computed. He claims an

efficiency of 82.2 per cent. While Woehler would probably obtain a higher current efficiency than Goodwin by employing a mixed electrolyte, yet the method of Woehler is open to criticism.

Goodwin's method gives us the efficiency for the actually available metallic calcium, while Woehler's efficiencies are too large, because, from my description of the nature of the deposited calcium, much of the metal was in a non-available form; that is, so intimately mixed with  $\text{CaCl}_2$  that it would be almost impossible to separate it mechanically or otherwise.

The method which I used in determining current efficiency was that of Goodwin, but I had to be very careful to completely break up the deposit in order to be sure that all of the  $\text{CaCl}_2$  was eliminated, for the specific gravity of the latter is so much higher than that of the metal as to very appreciably raise the apparent efficiency. Some of the pieces were even boiled in alcohol (anhydrous) in order to facilitate the removal of the  $\text{CaCl}_2$ .

The following four results, the best obtained, are submitted, all of which are for baths of 100 parts pure  $\text{CaCl}_2$  and 17 parts  $\text{CaF}_2$ .

#### Apparatus No. 3

- No. 1. Current, 76.4 amperes; time, 70 minutes; current efficiency, 67.65 per cent.
- No. 2. Current, 51.5 amperes; time, 57 minutes; current efficiency, 75.6 per cent.
- No. 3. Current, 45 amperes; time, 12 minutes; current efficiency, 84.6 per cent.
- No. 4. Current, 70 amperes; time, 10 minutes; current efficiency, 93.3 per cent.

*Chemical Changes in Electrolyte.*—Above was described the action of the bath during electrolysis, both when water was present and when the bath had been previously dehydrated. If the bath had been thoroughly heated for some time previous to the passage of the direct current, calcium was formed quite readily, other conditions being favorable. Now it will be remembered that the dehydration proceeded with the following successive results after the application of the heat to the  $\text{CaCl}_2 + \text{H}_2\text{O}$ : Firstly, steam came off; secondly,  $\text{HCl}$  fumes, then bubbles of hydrogen appeared all over the bath and lastly only the

yellow flames remained. As stated before, these yellow flames were never gotten rid of entirely under any conditions. They exist only in the very hottest part of the bath, i. e., at the cathode if direct current is used, and if alternating current is used only at the smaller electrode. For the most part they appear to be burning hydrogen but no doubt some other substances are present also.

In view of the fact that it is almost impossible to get such data as would give an exact insight into the chemical compo-

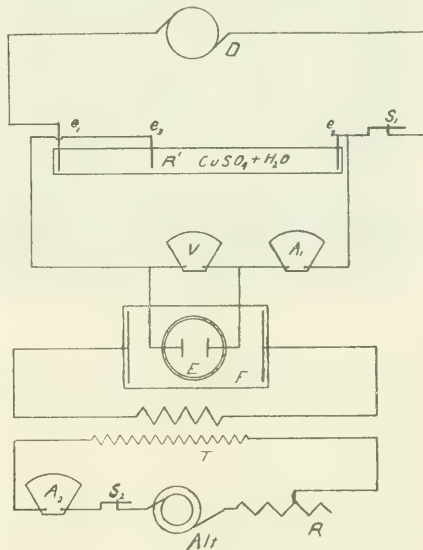


Plate VII.

Showing disposition of apparatus for obtaining decomposition voltage curves.

- E*—Electrodes in  $\text{CaCl}_2$  in Battersea crucible.
- E*—Liquid rheostat provided with three electrodes,  $e_1, e_2, e_3$ .
- S*—Switch.
- D*—Direct current dynamo.
- V*—Low-reading Weston voltmeter.
- A<sub>1</sub>*—Low-reading Weston ammeter.
- T*—Step-down transformer.
- A*—Ammeter.
- S<sub>2</sub>*—Switch.
- Alt*—Alternator.
- R*—Rheostat.

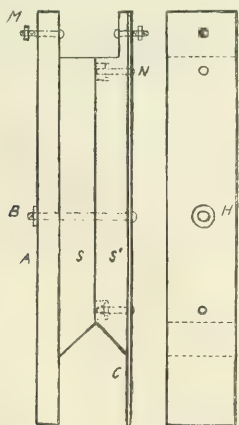


Plate VI.

- A*—Graphite anode.
- C*—Iron cathode.
- H*—Large hole through iron cathode.
- S* and *S'*—Soapstone separators.
- M*—Binding screw.
- B*—Bolt for holding pieces together.
- N*—Bolts for holding iron cathode to support *S'*.

sition of the bath, I can give only my belief as to what actually occurs. And in this I am influenced by the views of Woehler, who has made similar observations. Woehler claims that after the temperature of the bath has reached a certain value the  $\text{H}_2\text{O}$  which still remains begins to combine with the  $\text{CaCl}_2$  according to the following equation:  $\text{CaCl}_2 + \text{H}_2\text{O} = \text{Ca} - \text{OH}$ ;  
— $\text{Cl}$ .

This compound releases water with difficulty, and furthermore during electrolysis would probably react with the metallic calcium to form anhydrous oxychloride and hydrogen. This theory, while worthy of close consideration, does not explain why hydrogen bubbles and the yellow flames come off during the heating with alternating current. Nevertheless, the above equation probably states the condition of affairs somewhere nearly right. So far as the whole truth is concerned, we need much more data of a kind which is very difficult to get.

It is a well known fact, that if in the electrolysis of  $\text{NaCl}$ , the temperature of the electrolyte becomes too high the sodium will

redissolve in the electrolyte to form a hypothetical subchloride, and but little sodium will be obtained no matter how high the current density may be.

Such an assumption has been made by some regarding the electrolysis of  $\text{CaCl}_2$ :  $\text{CaCl}_2 + \text{Ca} = 2\text{CaCl}$ .

Richard Lorenz has shown that lead and zinc will dissolve in their respective chlorides if the temperature is raised to a

The two experiments just described do not prove absolutely that the dark particles are metallic calcium instead of  $\text{CaCl}$ ; but from the physical qualities, as metallic appearance and specific gravity observed, it was concluded that these particles must exist as finely divided calcium mechanically suspended in the bath when the latter is solidified.

Now from analogy it is very likely that calcium dissolves to some extent in  $\text{CaCl}_2$  at a high temperature the same as lead or zinc have been found by Lorenz to dissolve in their respective chlorides. However, there are grounds to believe that the solution of calcium in  $\text{CaCl}_2$  ought to be regarded as taking place in a manner exactly parallel to the solution of  $\text{CaCl}_2$  in  $\text{H}_2\text{O}$ , rather than to assume that a sub-chloride is formed. As such a compound has never been formed under any condition by any one so as to be recognized as a definite chemical compound, surely there is no reason to state without any qualifications that such a compound is formed in the electrolysis of  $\text{CaCl}_2$ . If we assume that the calcium is really soluble in the  $\text{CaCl}_2$ , while the latter is at a high temperature, as stated, we can also naturally infer that as the  $\text{CaCl}_2$  cools down that the solubility of the calcium in  $\text{CaCl}_2$  decreases and hence crystallizes out as it were.

In discussing the effects of dissolved metallic zinc or lead in their respective chloride baths which are undergoing electrolysis, Lorenz states that the metal acts as a depolarizer, and further, that no metal will be deposited at the cathode until the bath has become saturated with the metal.

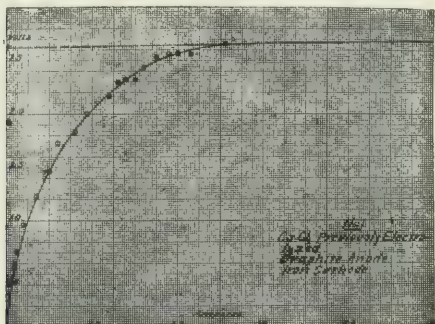


Plate VIII—Curve No. I.

certain value. The three factors upon which the phenomenon depends are given as follows: "Temperature of bath, volatility of the metal, and its solubility in the bath." He further states that this "metanebel," metallic cloud, as he terms the dissolved metal may be either (a) a real solution of the metal in its fused haloid salt, or (b) a mere pulverization of it in suspension. He prefers the former view.

I have called attention to the fact that those portions of the bath through which a direct current had passed for a considerable time were colored black. A piece of this black  $\text{CaCl}_2$  was found to decompose water, liberating hydrogen and forming a white precipitate of  $\text{Ca}(\text{OH})_2$  suspended in a clear solution, but leaving no black residue. This showed that the coloration of the  $\text{CaCl}_2$  was not due to the disintegrated carbon but to either finely divided metallic calcium or the subchloride.

Since  $\text{CaCl}_2$  is soluble in alcohol (anhydrous) and metallic calcium is not, a piece of the solidified electrolyte was placed in the solvent with the result that the  $\text{CaCl}_2$  was dissolved and a finely divided deposit formed at the bottom of the test tube. The alcohol was poured off and some water then poured on the

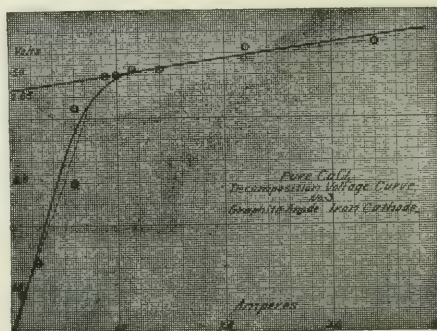


Plate IX—Curve No. III.

To be sure, there is some depolarization occasioned in the case of calcium also, but whatever may be the state of affairs for zinc and lead, it is certain that Ca can be deposited from a  $\text{CaCl}_2$  bath before it is saturated with the metal. This fact was proved while obtaining the decomposition voltage curve which follows. The electrodes used were two inches apart and placed in a  $\text{CaCl}_2$  bath which had never been electrolyzed before. There was much molten  $\text{CaCl}_2$  surrounding the electrodes and plenty of chance for circulation of electrolyte between electrodes. In several of these determinations of decomposition voltage, easily recognizable deposits of calcium were obtained, although the current used was small and the duration of its passage only a few minutes at a time. Indeed that most of the curves have well defined "knees" in them is sufficient proof of the fact. Curve II was taken for a  $\text{CaCl}_2$  bath which had metallic calcium suspended in it from previous runs, and it will be noticed that there is no well defined "knee" in the curve.

*Decomposition Voltage Curves.*—As just intimated, the study of the decomposition voltage curves which would be obtained under various conditions would throw much light on the best chemical composition of the bath as well as best physical conditions, correct temperature, etc., at which the electrolysis ought to be carried on for most successful results. Although

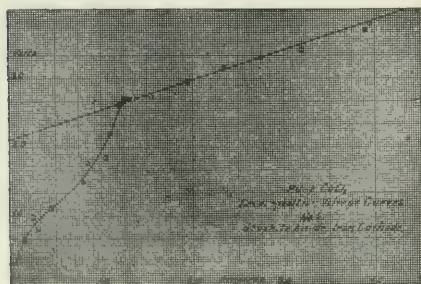


Plate IX—Curve No. II.

precipitate. Hydrogen immediately began coming off quite briskly. A drop of  $\text{H}_2\text{SO}_4$  was next added to the solution and instantly the whole black precipitate was changed to snow-white  $\text{CaSO}_4$ , and the heat developed from the reaction was sufficient to cause the ignition of the hydrogen liberated.



prevented by lack of time and the necessary pyrometer for determining temperatures, experiments along this line were not carried on as far as desirable. However, a few results have been obtained which are of at least some value. On Plate V is shown a diagram of the apparatus used, and on page 470 a description and data concerning same.

Details of electrodes for obtaining decomposition voltage curves are shown on Plate VI.

It must be borne in mind that the value of the decomposition voltage for a fused salt will depend not only upon the chemical composition of the electrolyte and its temperature, but also upon the nature of the electrodes used and to a slight extent upon their geometrical disposition with respect to each other.

In the experiments carried out a  $\text{CaCl}_2$  electrolyte only was used and in each case the data taken for the curve when the bath had just reached a nicely molten condition.

Curve No. II was obtained with an anode of graphite and a cathode of polished sheet iron, each 2.5 cm. (1 inch) square and separated 2.5 cm. (1 inch). After the current had been passed and the data obtained the electrodes were removed and examined. The anode, of course, was unchanged; while the cathode

resistance line to the Y axis we obtain 2.62 volts as the decomposition value.

Curve No. IV shows a very steep resistance line, due to the fact that only the tip ends of the electrodes were immersed in the molten electrolyte. The electrolyte was pure  $\text{CaCl}_2$ . Extension of the resistance line shows a critical voltage of about 2.65.

Since in many of the experiments performed calcium seemed to possess the power of forming a superficial alloy with the iron cathode, this fact may help to lower the critical voltage. (Theoretical 3.727.) If we could employ two electrodes which would be entirely inert toward the products of electrolysis and the electrolyte, we might reasonably expect to get results agreeing fairly closely with the theoretical value, if from this we also subtracted the voltage corresponding to the heat supplied to the  $\text{CaCl}_2$  to raise it from the ordinary temperature to the fusion point. This latter step is necessary since the heat of formation is given for solid  $\text{CaCl}_2$ .

However, the above values are probably approximately correct for electrodes of graphite and iron—the two electrode materials which would be used in the electrolysis of  $\text{CaCl}_2$  on an industrial scale.

#### DATA FOR DECOMPOSITION VOLTAGE CURVES.

##### Curve No. I.

Graphite anode, 2.5 cm. (1 inch) square. Iron cathode, 2.5 cm. (1 inch) square. Electrodes separated 2.5 cm. (1 inch). Bath of  $\text{CaCl}_2$  had previously been electrolyzed.

Volts.	Amperes.	Volts.	Amperes.
0.433	0.05	2.300	1.30
0.560	0.10	2.330	1.40
0.600	0.10	2.330	1.50
0.717	0.10	2.434	1.60
0.966	0.20	2.535	1.75
1.233	0.35	2.567	1.91
1.466	0.50	2.567	2.00
1.734	0.60	2.567	2.15
1.834	0.80	2.660	2.55
2.067	0.95	2.660	2.80
2.167	1.20	2.660	3.20

#### DATA FOR DECOMPOSITION VOLTAGE CURVES.

##### Curve No. II.

Graphite anode, 2.5 cm. (1 inch) square. Iron cathode, 2.5 cm. (1 inch) square. Electrodes separated 2.5 cm. (1 inch). Pure  $\text{CaCl}_2$  electrolyte.

Volts.	Amperes.	Volts.	Amperes.
0.10	0.025	2.7	1.3
0.40	0.10	2.7	1.35
0.65	0.15	2.725	1.55
0.95	0.25	2.95	1.95
1.1	0.45	3.15	2.35
1.5	0.80	3.30	2.75
1.75	0.85	3.40	3.20
1.85	1.05	3.70	3.90
2.2	1.10	3.80	3.95
2.6	1.20	4.10	4.30
2.7	1.25	4.20	4.50

#### DATA FOR DECOMPOSITION VOLTAGE CURVES.

##### Curve No. III.

Graphite anode, 2.5 cm. (1 inch) square. Iron cathode, 2.5 cm. (1 inch) square. Electrodes, 2.5 cm. (1 inch) apart. Pure  $\text{CaCl}_2$  bath.

Volts.	Amperes.	Volts.	Amperes.
0.95	0.10	3.05	1.15
1.25	0.25	3.05	1.40
2.00	0.60	3.25	2.20
2.70	0.60	3.30	3.4
3.00	0.90	3.75	4.15
3.00	1.00	3.90	5.00

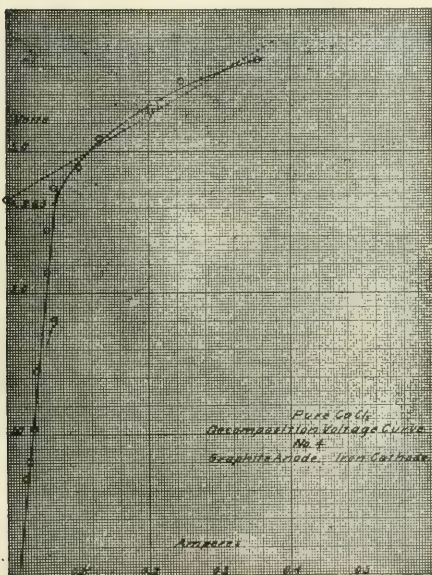


Plate XI—Curve No. IV.

showed no deposit of Ca, or any Ca-Fe alloy, it was appreciably corroded. By extending the resistance line we get 2.04 volts as the decomposition voltage.

Practically the same conditions are maintained in getting data for curve No. III, except for a slight increase of temperature as evidenced by the slope of the resistance line of the latter curve. The critical voltage for this curve is about 2.85 volts. An examination of the cathode after the run showed it to be covered with a thin bright deposit of calcium which decomposed water. After the calcium was dissolved off the iron was left in a soft corroded condition. No doubt, an alloy was formed with the iron at its surface.

As previously explained, curve No. I was obtained for a bath which had been previously electrolyzed and contained much metallic calcium in the electrolyte. If we extend the very flat

## DATA FOR DECOMPOSITION VOLTAGE CURVES.

## Curve No. IV.

Graphite anode and iron cathode. Only tip ends immersed in pure  $\text{CaCl}_2$  bath. Electrodes, 2.5 cm. (1 inch) apart.

Volts.	Amperes.	Volts.	Amperes.
0.30	0.0	2.15	0.05
0.44	0.0	2.45	0.05
0.55	0.0	2.75	0.06
0.70	0.025	2.90	0.10
0.81	0.03	3.10	0.13
1.05	0.03	3.25	0.20
1.10	0.03	3.50	0.24
1.45	0.04	3.65	0.35
1.755	0.04		

TRADE SCHOOL FOR THE LEATHER INDUSTRY.<sup>1</sup>

BY ALLEN ROGERS.

It is with extreme pleasure and gratification that I am permitted the honor of appearing before this joint meeting of the three American societies which stand for the growth, future development and higher aims of our leather industry. The coming together of such a representative body clearly signifies that we have passed beyond the rule of thumb period, realize the importance of technical education, and appreciate the benefit to be derived from coöperation. To-day, therefore, in my opinion, marks the beginning of a new era in our industrial advancement, and one which will go down in the pages of its history.

An attempt to enumerate all of the influences which have tended to bring about this condition of affairs would indeed be a difficult undertaking, but at the same time it might be of interest to note a few of the causes which have aroused us from a state of lethargy, and have made this wonderful scientific art one of the most important manufacturing interests of the country. The first great step in this direction was, no doubt, the introduction of chrome tannage by the Schultz process; this being a purely chemical treatment, paved the way for the application of chemistry along other lines. The second radical change has been the gradual breaking away from bark tannage, with the consequent replacement by liquid and solid extracts. The third advance has been due to the knowledge gained in the manufacture and use of mineral and sulphonated oils, either employed alone or in conjunction with vegetable, animal, and fish oils. The fourth cause should be ascribed to the perfection attained in the manufacture of leather-working machinery. Among the many other causes responsible for this growth should be included the application of chemistry. Indeed, we cannot give too much credit to those who have labored so strenuously to solve the many difficult problems which have constantly confronted them. Let it be borne in mind that the American Leather Chemists' Association, as well as the International Leather Trader Chemists' Association, have done and are still doing a work which should gain for them the everlasting gratitude of the tanner, the currier, the shoe manufacturer, the other users of leather, and the public at large.

And last, but by far not least, should be mentioned the manufacturers themselves. These men of sterling character, who have worked by day and planned by night to bring order out of chaos, who have been to the leather industry what Lavoisier was to the science of chemistry: The organizers and producers of results.

We have come now, however, to the fork in the road, and it remains for us to choose the path. On the one hand is the old beaten trail, full of pitfalls and obstructions, while on the other hand we see a smooth, wide thoroughfare, scientifically constructed, freely oiled with the lubricant of technical skill, and

with no signs to intimidate those who desire to travel faster than the regulated speed limit.

Which road will be our choice? This question is easily answered when we consider that we are traveling in a modern conveyance, and not with the ox team of our grandfathers. To travel this road, however, we must be skilful in the manipulation of our vehicle, so as to avoid the danger of an upset should we lose control of the steering gear. Equally disastrous would be the result of a rear-end collision should we go too slow. We must, therefore, keep up with the procession or drop out of the race.

As we hesitate in our decision the cloud of doubt slowly rises, exposing to our vision the wonderful truth that others before us have already taken the modern route, and that weeds and bushes are growing in the beaten trail. With the dawning of this fact upon our senses we take new courage, so with a steady hand on the lever and a sharp eye on the road, we start out in pursuit of those who are ahead, trusting that with our knowledge, skill, and energy we will eventually gain the lead.

Thus it is that American manufacturers have been standing at the fork in the road. They have seen the new route, but have hesitated until they were convinced that England, Germany, France and Italy were no longer following the beaten trail. There are many, however, who have realized this condition for several years, and many more also who will not realize the condition for years to come; but let us be thankful that it has been realized and that we are headed in the right direction. Without throwing any bouquets at himself, the speaker has appreciated for some time that eventually we would break away from the old régime. That his dreams might be realized seemed possible when in September, 1905, he was appointed to his present position, and he could attempt the inauguration of a course in tanning which would be to America what some of the foreign schools are to their respective countries. That this attempt has not been futile is evidenced by the fact that twelve of our graduates are at present employed in the leather industry. Yet it has not been all smooth sailing by any means, and there have been times when the undertaking seemed hardly worth the candle. But we are told to cast our bread upon the water, and I feel in this instance at least it has returned again a thousandfold, for there is no doubt that our small beginning had much to do with the recommendations of the committee that the proposed Tanners' Institute be founded at Pratt Institute. It is, therefore, of Pratt Institute, its methods, its aims, its past, its future, and what it hopes to accomplish for the leather industry that I wish to speak.

The founder of this institution, Mr. Charles Pratt, was born of parents in moderate circumstances, and was deprived in his youth of the advantages of an education. As a young man he worked at various trades, and finally became stillman in one of the oil refineries. While engaged in the duties of his occupation he noticed that if a certain fraction of the distillate was separated he obtained the highest grade of illuminating or kerosene oil. Taking advantage of this observation, he started in a small way to put the product on the market, with the result that Pratt's Astral Oil became so widely known that the business rapidly developed into one of vast proportions. In time the Pratt refinery became part of the Standard Oil Company. As prosperity smiled upon him, Mr. Pratt saw the opportunity of realizing his great ambition, and that was to establish a school which should give to others what had been denied him in his own youth. His chief aim was to reach out and help all practical workers, and being a man of wide experience, he fully appreciated the shortcomings of the ordinary schools in this connection. He, therefore, sought for some means whereby young men and young women might be given a liberal education, and at the same time become proficient along some definite line of work. Although he met with but very

<sup>1</sup> An address delivered at the meeting of the Leather Chemists' Association, Chicago, October 6, 1910.

little sympathy, he was not shaken in his belief, so in 1887 he founded the institute which bears his family name. At the opening of the school in the fall of 1888 there were no definite plans arranged as to the nature of the courses to be followed, it being his idea to first learn what the students desired, and then endeavor to give it in the most practical and systematic manner. On the opening day there appeared twelve students, each one wanting something different from the rest. They were told that the necessary teaching force would be secured to meet all of their demands, and in a few days the work was undertaken.

It would be too long a story to follow the growth and development of the institution, suffice it to say that since 1888 the enrolment has increased from twelve students to over 4,000, and during that time instruction has been given to over 65,000 individuals. During the early years of its growth Mr. Pratt gave a large part of his personal time and attention to its management, and since his death the work has been carried on by his five sons and one daughter, who have liberally added to its endowment.

The range of subjects covered may be judged from the fact that at present there are offered over sixty distinct courses, many of them day courses and others evening courses. The students enrolled are drawn from nearly every state in the Union, and from a number of foreign countries. It requires nine different buildings to house these classes, and they are taxed to their full capacity.

It is a significant fact that Mr. Pratt did not, in his will, lay down any hard and fast rules for the institute. The trustees have, therefore, made changes in the courses whenever they seemed necessary, but have never changed its purpose, though this is also in their power. It is owing to this elastic condition of affairs, and to the increased demand for young men with technical training, that it was deemed advisable to introduce a course in applied chemistry. Consequently, in September, 1905, the work was undertaken, at which time the speaker accepted the position as instructor in charge of industrial chemistry, and was told to organize his course and equip his laboratory for practical instruction. This may seem a very simple proposition, but rest assured it was no small task. Being an entirely new departure in this method of teaching the subject, there was no school which could be visited in order to gain information. It was, therefore, largely a matter of originality, although our simple creed, as outlined by the founder, was constantly before us. That simple creed is:

Show men how to do something, and then insist that they do it as well as honestly, as economically as it is possible to be done.

Show men why certain combinations produce the desired results, see that they understand the simple principles and apply them to their work.

Consequently, in order to teach young men the methods employed in the manufacture of commercial products, it is necessary to bring them in as close relationship as possible with the actual working conditions. This method shows them the how. The why is gained by class-room instruction. To carry this idea into practical operation, we started out with five miniature factories, equipped in such a manner as to be able to manufacture on a fairly large scale, each plant being a unit by itself and worked independently of the others. They are as follows: Chemical works, soap works, tannery, dry color and paint works and dye works.

What the institute desires is to meet the needs of the large number of young men who cannot afford the time or money for a four-year course with college requirements, and hence is made but two years in length. It is designed especially to give the necessary technical knowledge and practical training to those who wish to become foremen, superintendents or heads of

departments in the important chemical industries. We are not, as some suppose, a trade school; that is, we do not claim to graduate men who are fitted to do only one kind of work. On the other hand, we are far removed from the ordinary technical school or university. Although we may teach the same or similar subjects as given in trade or technical schools, we approach them in an entirely different manner, while the attitude of our students toward their work is also quite different. Our field, therefore, may be said to lie half way between the two.

The method of selecting our students is one which is characteristic of Pratt, and may be of interest to mention at this time. On appearing for examination, the young man is given a personal interview by the instructor in charge of the department. This interview constitutes the major part of the examination, as by it we judge his mental and physical ability to handle the course. He is then given a test in English and arithmetic. This you will note is quite a bit different from college requirements. Having been admitted to the course, his first year is devoted to the study of general chemistry, qualitative analysis and quantitative analysis, together with the necessary amount of physics, mathematics and mechanical training. The last two subjects extend over two years and include mechanics, strength of materials, steam and power transmission, pattern-making, forge, foundry, machine work and design.

In the second year of the course the student is brought into contact with commercial processes, the major part of his time being devoted to industrial chemistry and technical analysis. During the fall term one hour each day is given over to class-room instruction in inorganic industrial chemistry, by means of which he becomes familiar with the details involved in the various branches of industry. Not only is he made familiar with the processes and relationship which exist between them, but is shown where chemical knowledge and control are very beneficial, and often absolutely essential. In the winter term the class-room instruction covers general organic chemistry, while the spring term is devoted to organic industrial chemistry. On completing each industry one or more trips are made to such factories as best illustrate the points which have been studied, thus more firmly fixing the knowledge gained by class-room instruction.

It is on our laboratory work, however, that we place special emphasis, as it is through this method of training that we hope to prepare young men to fill the positions mentioned above. At the beginning of the school year one man is assigned as foreman of the chemical works, and is given four of his classmates as assistants. He is instructed in this assignment to make an estimate for the manufacture of some chemical; to see that his machinery is put in perfect condition; to inspect his shafting, belts and motors; to see that everything is in order, and that his factory is kept clean. In order to make his estimates in an intelligent manner he has all raw materials tested out by the laboratory force, takes into consideration the cost of raw materials, freight f. o. b. New York, wear and tear of machinery, interest on investment and cost of containers. All of these details are taken into account before he attempts to make the product, for he must be satisfied that it can be made at a profit. Having determined that it is a profitable operation, he endeavors to produce as much high-grade material as possible. Although the student may be called upon in after-life to manufacture chemicals, the training in this plant is very beneficial, as it teaches him to handle the steam-jacketed kettle, vacuum pan, vacuum filter, vacuum pump, filter press, and centrifugal machine. Having spent one week at this kind of work, the entire crew are transferred to analytical problems, and a new gang takes their place.

When the chemical works have been in operation for about three weeks the first gang are assigned to the soap factory, the second in line becoming foremen. Here the same idea is



carried out, with the result that the students become familiar with the various processes employed in the manufacture of soap. Starting out with the raw materials they follow the numerous operations even to that of wrapping, boxing and shipping. During the past year we made over thirty-five hundred pounds of toilet soap in our miniature factory. Next in order comes our miniature paint factory, in which during the past year we made about four hundred gallons of ready-mixed paint. In this connection I might add that owing to coöperation with the American Society of Testing Materials we have arranged to grind one hundred and sixty different kinds of white paints during the coming year, all of which will be tested out on fences erected for the purpose. To carry out this word and increase our efficiency we have added two twenty-inch burr-stone mills, a roller mill and post mixer, making an equipment with a maximum capacity of one hundred gallons per day.

In our miniature tannery the same procedure holds good as for the chemical, soap and paint works. The equipment for this plant consists of three pits, one paddle, one drum, a union splitter, one set of buffing wheels, rolling and glazing jack, slating table, and beams, with the necessary tools for hand work. During the past year we tanned 350 sheepskins, 45 calfskins and several hides. What we plan to add to this equipment I will mention later.

Having given a partial outline of our methods as they now exist, before taking up what the future may have in store for us, I would like to mention a few facts which show the phenomenal growth of this department. In the fall of 1905, when the course was started, there were eight men who applied for chemistry. By taking men who had been refused admittance to other courses, the class was finally made up to twenty-seven. In 1906 about fifteen applied for chemistry, and that year the class was made up to thirty. In 1907 there were twenty-five applied for chemistry. In 1908 about the same number applied as the previous year. In 1909 forty applied for the course, and the class was made up with thirty-five of them. This year there were fifty-one applied for the course in chemistry, of which we took thirty-three, making the class up to our limit of thirty-five, with two men who were required to repeat the first year. I think that you will agree with me that this is quite a rapid growth. Out of the twenty-seven admitted to the first class we graduated sixteen. Of the thirty in the second class we graduated seventeen. The following class graduated eighteen. Last June we graduated twenty-three, while next June we expect to graduate twenty-three. These figures are interesting, as they tend to prove the old adage, "You can lead a horse to water, but you can't make him drink." That is to say, we admitted men to our first three classes who were not desirous of taking the course, and with the consequent result that our mortality was very great. That we have gained somewhat of a reputation in the past five years, and that our graduates as a rule have made good, is indicated from the fact that of the twenty-three men who finished the course last June there were twenty-one placed in good positions before graduation. Of the seventy-four graduates and eight special students who have taken this course, there are seventy-eight engaged at present along chemical lines. Those of you who have read the report of the Committee on the Tanners' Institute are aware that after considering the advantages of several institutions of learning, all agree on Pratt Institute as being the most desirable school for the kind of work to be undertaken.

Although we have not decided upon the details of the courses to be offered, I feel justified in presenting a few tentative suggestions, and trust that there may be many valuable points brought up in the discussions which I hope will follow. From our experience in the past, it is safe to assume that there will be three types of men to apply for this work. The first class

will be those who are at present engaged in the industry and want to obtain some knowledge of the theoretical and technical side of the subject. The second class will be those who are graduates from technical schools and universities, who desire to know something of the practical operations involved in the manufacture of leather. The third class will be those who have taken our two-year course in Applied Chemistry, and wish to spend an additional year in a more advanced study of the practical, technical and theoretical problems. There is also another class of men who will want to follow some special line, such as coloring beamhouse practice, chrome tannage, etc. This last type, however, presents a difficult problem, and one which I think at present would be almost impossible to handle. It therefore seems evident that we must present two courses—one in which the principal feature is theory, and the other in which the principal feature is practice. We must consequently start out with a definite object in view, and so organize the work that it will do the greatest good to the greatest number, and above all we must have system. The courses which it would be most natural for Pratt Institute to offer would be those in which the practical and theoretical are so blended as to fill the needs of the above-mentioned classes. It would thus appear wise to offer two courses, each being one year in length.

Course A should be designed for men who have already been employed in the leather industry. What these men want is a broader knowledge of the practice of tanning, together with an idea of the most important scientific principles upon which the industry rests. Some of the subjects which should be included in this course would be the following:

- (a) Elementary principles of chemistry as related to the tanning industry.
- (b) Chemical laboratory practice in conjunction with the above.
- (c) Lecture course in industrial chemistry covering such industries as are closely related to tanning.
- (d) Laboratory practice in industrial chemistry covering such subjects as soap-making, boiling of oils, dyeing, etc.
- (e) Technical analysis, such as water, coal, oils, fat, egg yolk, extracts, barks, etc.
- (f) The principle and practice of tanning, using an improved text on the subject.
- (g) Practical tanning and finishing in school tannery.
- (h) Brief course in mechanical drawing.
- (i) Power plant operation, and mechanical transmission of power.

Course B should be designed for men who have graduated from a four-year chemical course, from our two-year day course in applied chemistry, and for other men who are properly prepared. Some of the subjects which might be included in the course would be the following:

- (a) The principles and practice of tanning, using an approved text.
- (b) Practical tanning and finishing in school tannery.
- (c) Technical analysis, including such substances as water, oil, grease, fat, wax, egg yolk, extracts and barks.
- (d) Chemical research. This would include the investigation of such problems as constantly arise, and the publication of the same from time to time.
- (e) Industrial chemistry: A lecture course covering such industries as are closely related to tanning.
- (f) Industrial laboratory practice, including the manufacture, use, and testing of dyestuffs, soap-making, oil-boiling preparation of varnishes, finishes, etc.
- (g) Problems in the design and construction of tanneries, with arrangement of power plants and equipment.
- (h) Power plant operation, including electrical and mechanical transmission.

For the benefit of all students there should be conducted during the year a series of lectures, which should be given by men who are specialists in their line of work.

The equipment required for the two courses would, of course, be identical, and much of the practical instruction for both groups would be the same. Each group of men would profit by the close association with the other. The men from the factory would learn much from the men of scientific training, while the men with theoretical knowledge would become broader by working shoulder to shoulder with men of practical experience. In the technical and theoretical portion of the work, however, the courses should be kept entirely separate and distinct.

The plans as just outlined, therefore, offer three courses of different length:

(I) A one-year course for those who have had practical experience, and cannot afford the time or money for the longer courses.

(II) A three-year course, consisting of two years in our day course in applied chemistry, and one year in the special course in tanning.

(III) A five-year course, consisting of four years in some technical school or university, and one year in the special course in tanning.

In order to carry out the plans for this course we have been engaged, during the summer, in making extensive alterations in our chemistry building. We have provided for about six times as much floor space as originally occupied by our school tannery, have greatly enlarged our analytical laboratory, and added materially to our other industrial plants. To facilitate the instruction in tanning we have planned for the installation of seven more pits, an 8-foot drum, a 4-foot paddle, fleshing machine, shaving machine, staking machine, a new finishing room and two drying rooms.

In order to properly carry on the work, it will be necessary for us to increase our teaching force, which would require at least two more men. One of these men should be a high-grade tanner and finisher who has had practical experience in all of the different branches of the industry. The other man should be a well-informed chemist who has had both teaching and practical experience. This addition with our present staff of five in the chemical department would amply provide for the instruction which would be necessary. In the School of Science and Technology, of which the Tanning Course would be a part, we have nearly fifty instructors, so that there would be no difficulty in the other departments.

To permanently provide for the annual expenses of these additional salaries, to cover the operating expenses, the maintenance of equipment, the heat, light, janitor service, etc., an endowment of something over \$100,000 would be necessary on the part of Pratt Institute.

That the Institute is deeply interested in this project is evidenced from its proposition to the Tanners' Association. That it is not from any financial consideration which might accrue is also apparent. We are taking it up because we believe that the tanners are interested, and that it is a field in which we hope to be of service.

That the tanners are very much interested in the founding of a school where young men may be trained along the proper lines needs no proof. The establishment of a fund for the promotion of research, for scholarship, for publications and other uses will be of the greatest benefit to the advancement of the industry. Above everything else, however, we must have coöperation, encouragement, and support. Let me impress upon the National Association of Tanners, the American Leather Chemists' Association, and the Extract Manufacturers' Association, as well as the manufacturers of dyestuffs, chemicals, machinery, oils and specialties that we need your help. For

if we are to succeed we must join our forces so as to work in unison and harmony to achieve the one great end.

ALLEN ROGERS.

#### CAST COPPER OF HIGH ELECTRICAL CONDUCTIVITY.<sup>1</sup>

By DR. E. WEINTRAUB.

The production in the foundry of pure copper castings mechanically sound and possessing an electrical conductivity comparable to that of pure forged copper has been an important problem ever since the development of electrical machinery and apparatus. The literature as well as the patent files are replete with descriptions of methods for the accomplishment of this result. Secret compositions, warranted to give high conductivity copper, were and are being sold to foundrymen, and there are but few foundry foremen to be met with who do not claim to have some time or other obtained the desired result by adding "phosphorus" or similar material. Obstinate, however, the casting of high conductivity copper refused to make its entrance in the foundries and we may assume that there were good reasons for it.

The cause of the difficulty of producing sound pure copper castings has been sufficiently well understood for a long time. Molten copper has the property of dissolving gases such as oxygen and of setting a part of these gases free on cooling. This produces pin-holes and even big cavities. The casting obtained is therefore mechanically unsound and has naturally a low electrical conductivity.

The elimination of these dissolved gases presents but little difficulty. It is sufficient to add one of the well-known deoxidizers such as zinc, magnesium, phosphorus, etc., in small quantities to bind the oxygen chemically. Copper castings free from blow-holes are thus easily produced. The electrical conductivity of the copper thus produced is, however, as a rule, low; and this because all the deoxidizers used had also the property of combining with copper, and the remarkable rate at which the conductivity of copper drops when small amounts of impurities are alloyed with it is well known. The amount of oxygen dissolved in copper during the process of melting is a variable quantity and is distributed throughout the whole mass. It is therefore practically impossible to add the deoxidizer in such a way as to eliminate oxygen completely without, at the same time alloying it to a certain degree with the copper. Accordingly the conductivity of the resultant product was a matter of accident. In the laboratory sometimes good results were obtained but they were hard to duplicate and the transfer to the foundry was always a disastrous experiment.

It seemed to me that what was needed for the solution of the problem was the finding of a deoxidizer which would have no affinity for copper (at least at the melting point of the latter) and which, therefore, could be added in excess with impunity.

While carrying on the work of the isolation of the pure element boron, and its fusion, the lack of affinity of this element for copper has forcibly impressed itself on my mind. Boron has, at the melting point of copper, a great affinity for oxygen, nitrogen, etc., and it occurred to me, therefore, that boron ought to be the ideal substance for deoxidizing copper.

Pure boron as prepared by methods described by me in paragraphs 2 and 4 of my article<sup>2</sup> can, by this time, be produced in large quantities and is rather inexpensive for uses based on its electrical properties. For casting copper, however, its price would probably be too high.

In the course of the investigation mentioned I had prepared, however, an amorphous powder which contained as essential impurity only a certain percentage of oxygen and which I termed "boron suboxide." This substance is prepared by a

<sup>1</sup> An address read before the Chicago Meeting, American Electrochemical Society, October 13, 1910.

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **16**, 165.

modification of the reduction-process of boric anhydride by magnesium. Obviously for the purpose of eliminating oxygen from copper without introducing any impurity capable of alloying with copper, this boron suboxide would be as good as pure boron or perhaps better on account of its being obtained in form of a very fine powder.

This substance was used in the first experiment. The very first attempt was successful. A perfectly sound bar was obtained with a conductivity of 94 per cent. 0.1 per cent. of the weight of the copper was added. Further experiments showed that the amount of boron suboxide could be reduced to  $1/50$  per cent. and also that the addition of a large excess, say of 1 per cent., did not diminish the conductivity or change in any way the mechanical properties of the cast copper.

Here was, therefore, a method which could be put into the hands of any foundry man and which would always give good results provided the copper (ingots or scrap) melted down was pure metal.

A further simplification could, however, be introduced into the process. The reduction of boric anhydride by magnesium, the first being in excess, gives a product containing magnesium borate, boric anhydride and boron suboxide. While the last one is the active agent, the first two are harmless. In fact, the presence of boric anhydride and magnesium borate is even an advantage as the addition of a larger mass of material makes the operation easier; also the boric anhydride would probably dissolve the copper oxide and bring it to the surface as copper borate. It is therefore unnecessary to submit the direct product of the reaction to chemical treatment for the purpose of isolating the boron suboxide. It is sufficient to grind up the mixture into coarse grains and use an amount of it which contains the necessary amount of boron suboxide.

The foundry practice at present is to add 1 per cent. to  $1\frac{1}{2}$  per cent. of this material which is equivalent to 0.08 to 0.1 per cent. of boron suboxide.

The properties of the material obtained are as follows:

The electrical conductivity obtained can be as high as  $97\frac{1}{2}$  per cent. if the copper melted down is perfectly pure. In the foundry, where the scrap copper which is melted down cannot always be very carefully selected, a conductivity of 91 to 95 per cent. is obtained and a guarantee of 90 per cent. is at present given.

The resultant casting is readily machined; fears which were entertained on this subject did not materialize and the engineers using the material have not complained on this account.

The mechanical properties are as follows:

Tensile strength.	Elastic limit.	Elongation.	Reduction in area.
24350	11450	48.5%	74.4%

Castings are being made of all shapes and sizes with no more difficulty than in the case of brass. Sand and iron moulds can be used and for standard articles the latter are preferred.

The use of cast copper lies in two different directions: 1. Replacing forged copper. In this case a great saving in cost is often obtained. (2) Replacing alloys of copper. The gain in conductivity allows the reduction in bulk and thus a saving in material.

The use of this material is spreading as the engineers get better acquainted with it and is already of very considerable magnitude. It is interesting to note that in spite of the fact that cast copper has lower conductivity than forged copper, in many cases, as for instance, in case of current transformers, the effect of higher conductivity is obtained by substituting it for forged copper. This is due to the fact that in casting a chance is given to eliminate riveted screwed or soldered joints whereby a number of poor contacts are avoided. Not only this but the elimination of joints often insures a better operation.

The cost of the boron added is small; at the present prices

of magnesium and boric anhydride the cost per pound of copper is less than 0.73 of a cent.

The success with "boronizing" copper, as it is now called in the foundry, suggests new lines of work which I have taken up lately.

Among these I mention:

First, the addition of boron to different copper alloys.

Second, the replacing of the poling operation in the process of refining copper by a "boronizing" operation.

In conclusion, I want to express my appreciation of the excellent work done by my assistant, F. A. Kroner, without whose energy and foundry experience the technical and commercial success of the process described would have been greatly delayed.

CONTRIBUTION FROM THE RESEARCH  
LABORATORY, GEN. ELEC. CO.,  
WEST LYNN, MASS.

## NOTES AND CORRESPONDENCE.

### BAKELITE AND RESINIT.

*Editor Journal of Industrial and Engineering Chemistry:*

On page 441, you publish a consular note about Resinit Compound. For the information of your readers, I beg to mention that the use of sodium sulphite, ammonium sulphite, tertiary sodium phosphate, sodium acetate, and all bases or basic salts, with which these Resinit compounds are made, as well as the impregnation of wood and other cellular or fibrous materials like infusorial earth, starch, etc., is broadly covered by my United States Bakelite patents:

No. 939,966, filed Jan. 28, 1909. Issued Nov. 16, 1909.

No. 941,605, filed Feb. 1, 1909. Issued Nov. 30, 1909.

No. 942,699, filed July 13, 1907. Issued Dec. 7, 1909.

No. 942,700, filed Dec. 4, 1907. Issued Dec. 7, 1909.

No. 942,808, filed Oct. 26, 1907. Issued Dec. 7, 1909.

No. 942,809, filed Oct. 15, 1907. Issued Dec. 7, 1909.

No. 942,852, filed July 13, 1907. Issued Dec. 7, 1909.

No. 949,671, filed Feb. 18, 1907. Issued Feb. 15, 1910.

No. 954,666, filed Oct. 15, 1907. Issued Apr. 12, 1910.

No. 957,137, filed Oct. 8, 1909. Issued May 3, 1910.

Several other patents are pending here and abroad, and will be published later on.

For further information, I may tell you that the former manufacturers of Resinit have discontinued the manufacture of this article, and have purchased an interest in the Bakelite Gesellschaft, m. b. H., in Berlin, who are the owners of my European patents, and who, for certain purposes, will supply also Resinit compounds.

On this occasion, permit me to state that the first public mention of Resinit was made in Heidelberg, about one year after my French patents were published, and several months after I had read my paper on Bakelite before the American Chemical Society, and after it had appeared in this Journal, and translations thereof had been published in Germany and other foreign countries.

I am pleased to state that since a few days, my United States, Canadian, Mexican and Japanese patents have been acquired by the General Bakelite Company, 100 William Street, New York City, and that henceforth, Bakelite and the raw materials thereof will be obtainable from that source.

Respectfully yours,

L. H. BAKELAND.

### TRIBO-LUMINESCENCE.<sup>1</sup>

The term "Luminescence" has been applied to the light which is emitted by various substances at a temperature much lower

<sup>1</sup> Read at Chicago Meeting of Am. Electrochem. Soc., October 13-15, 1910.



than that which is necessary to show visible incandescence, as illustrated for example in the light of the firefly, decaying wood, and many natural and artificial mineral compounds.

The general phenomenon of luminescence has been divided into several classes by Dr. Sylvanus P. Thompson, as shown in the following tabulation which is copied from his book entitled "Light Visible and Invisible," page 175 (1893).

Phenomenon.	Substance in which it occurs.
1. Chemi-luminescence.....	Phosphorus oxidizing in moist air; decaying wood; decaying fish; glow-worm; firefly; marine organisms, etc.
2. Photo-luminescence	
(a) Transient: Fluorescence....	Fluor-spar; uranium-glass; quinine; scheelite; platinum-cyanides of various bases; eosin and many coal-tar products.
(b) Persistent: Phosphorescence..	Bologna-stone; Canton's phosphorus and other sulphides of alkaline earths; some diamonds; etc.
3. Thermo-luminescence.....	Fluor-spar; scheelite.
4. Tribo-luminescence.....	Diamonds; sugar, quartz; uranyl nitrate; pentadecyl-paratolyketone.
5. Electro-luminescence	
(a) Effluvio-luminescence.....	Many rarefied gases; many of the fluorescent and phosphorescent bodies.
(b) Kathodo-luminescence.....	Rubies; glass; diamonds; many gems and minerals.
6. Crystallo-luminescence.....	Arsenic acid.
7. Lyo-luminescence.....	Sub-chlorides of alkali metals.
8. X-luminescence.....	Platinocyanides; scheelite; etc.

Tribo-luminescence, to which the present remarks particularly refer, is the property possessed by certain bodies of emitting light when rubbed or scratched.

A number of natural mineral exhibit different degrees of this property, an interesting investigation of which is described in a paper by Mr. Wallace Gould Levison, published in *Science*, N. S., Vol. XIX, No. 491, pp. 826, 827.

A simple but rather faint illustration of the phenomenon may be easily produced by rubbing together two lumps of white sugar in the dark.

While experimenting in the production of fluorescent and phosphorescent materials several years ago, the writer accidentally discovered that one of his preparations exhibited tribo-luminescent properties, and two or three subsequent trials led to improved results. As an easily prepared artificial product of this kind does not appear to be generally known, some brief directions for making it may be of possible interest.

The following mixture was selected as the best after a series of experiments.

Zinc carbonate (C. P.).....	70 parts by wt.
Flour sulphur.....	30 parts by wt.
Manganese sulfate.....	trace.

The zinc carbonate in fine powder should first be mixed with the flour sulphur. Then a small particle of manganese sulphate should be dissolved in distilled water and enough of the solution added to the powdered materials to make a thick cream. After being thoroughly triturated in a mortar, the mixture can be poured into a shallow glass or earthenware dish and allowed to dry at a gentle heat. When quite dry it should be again reduced to a fine powder, and packed *hard* into a porcelain or Battersea crucible with a tight cover, and subjected to a bright red heat for twenty minutes. The mixture shrinks considerably and sinters together into a stone-like mass, which possesses the peculiar property of tribo-luminescence to a marked degree, so that when scratched with a knife blade or sharp point, it emits a train of minute sparks showing a yellowish light. This light appears to have little or no heating effect as it will not ignite any inflammable vapor or gas, so that in this

regard, it differs essentially from the light and sparks produced by striking together flint and steel, or the scratching of a pyrophoric alloy of iron and cerium.

W. S. ANDREWS.

#### RAPID SAPONIFICATION OF FATS FOR TITRE DETERMINATION.

There have been many detailed methods proposed for the rapid and complete saponification of fats for titre work, all of which divide themselves into two classes, one the water-caustic method and the other the alcoholic-caustic method.

The water-caustic saponification is slow and liable to be incomplete unless well stirred. Where strong caustic is used over a flame, there are the objections of scorching the soap.

In alcoholic saponification, we have the expense, the danger of fire and necessity of expelling all alcohol. It has been decided to try out some less volatile solvent. Glycerine has been used for saponification, but never for titres. The method proved so rapid, easy and complete, that it was thought advisable to give a detailed description of same.

Experiments were tried with C. P. Glycerine (95 per cent.). This was found not to "take hold" of the stock well, especially when the fat was neutral. Also some tedious foaming occurred and the 5 per cent. of water had to be expelled to get saponification to start. H. G. glycerine was substituted. The following gives the details of method as finally adopted.

About 120 grams of H. G. glycerine are placed into a 6½" porcelain casserole, a stick and a half or about 25 grams of caustic potash added and the whole heated over a flame. The potash dissolves very easily; now the fat is added (100 grams) and stirred while heating over flame. In a minute the fat dissolves in the caustic. Slight foaming occurs in the case of pure and refined fats. Heating is continued until a quiescence appears, shown when caustic solution and fat become a homogeneous mixture, indicating complete saponification. This point is not indicated so well by low-grade fats. In this case 10 to 15 minutes' heating was always found to complete same. Now the melt is taken off the flame and about 15-30 cc. cold water added, bit by bit, from a wash bottle, allowing each foaming to subside. Dilute acid is added to break up the fatty acids. The fatty acids precipitate in a milky form so that it only takes slight heating to coalesce them into a layer.

It is important not to get too much water into the melt after saponification, as this would hydrate the soap and when the acid is added, it would take much longer to boil out same so as to get clear fatty acids. At times we have been able to add just enough water so that when acid was added, the heat generated did the boiling out and fatty acids were clear. Insufficiency of water will cause the formation of too much heat when acid is added to the melt. The acid must be added from the cylinder in small quantities, stirring in each addition. Now a larger quantity of hot water is added and the whole placed on steam bath ready for washing. The whole operation takes less time than it does to write it. We have completed the operation of saponification and breaking up soap in ten minutes on a single sample or in one hour and forty minutes on nine samples of high-grade stock.

There is no long and tedious stirring of semi-solid soaps or prolonged dissolving of same in water and no long boiling out as in water and alcoholic methods. The method requires some experience and care in the case of low-grade stocks.

It has been tried out thoroughly against other methods of saponification and found to hold good concordance. The cost of the glycerine is at most three and a half to four cents per liter. The saponification is rapid and complete and the breaking up of the soap likewise rapid. It requires a little experience to strike the right point of dilution of the melt, but this is soon acquired by the operator. It is excellent where factory con-

trol requires rapid work. The method has been checked against the other standard methods by Mr. W. C. Marckworth and Mr. H. C. Knight, 1st and 2nd assistants. CHAS. V. ZOUL.

THE PROCTER AND GAMBLE LABORATORY,  
IVORYDALE, OHIO

#### IMPROVEMENT OF THE WILEY METHOD FOR DETERMINING THE MELTING POINTS OF FATS.

During the course of an extended investigation on the chemical and physical properties of animal fats the writer had occasion to use the Wiley method for determining the melting point of fats. This exceedingly ingenious method was found difficult of manipulation under all but perfect conditions. However, with a few modifications the operation may be considerably improved.

As is well known to all who have had experience with this method the main difficulty is encountered in securing fat disks perfectly free from occluded air. During the course of the determination, the smallest trace of air is sufficient, by its expansion on heating, to carry the fat disk to the surface of the liquid and thus ruin the determination. With high-melting fats, as tallows, the difficulty is especially great on account of the great change in temperature and therefore great expansion of the air. It is true that the number of air bubbles may be appreciably decreased by preparing the fat disks on ice floating in cold, recently boiled, distilled water. If the water is not near the freezing point, some of the ice will melt and thus introduce air into the water. Some ice used was found to be so full of occluded air that even with these precautions fat disks prepared on it invariably were found to be useless for a melting-point determination.

With a view of correcting these difficulties the writer prepared fat disks by dropping the melted fat on cold mercury. By proper adjustment of the height from which the fat is dropped, together with proper control of the temperature of the fat and mercury, disks of very regular shape were obtained. When thoroughly cool and hardened, they were removed with a cold steel spatula and thrown into a beaker containing cold, dilute (50 per cent.) alcohol. The beaker was then set in a vacuum desiccator and the air exhausted until bubbles ceased to be given off. Usually this was obtained in less than an hour. Disks thus prepared were found to be always free from occluded air and satisfactory in every way for the determination.

HARRY STEENBOCK.

LABORATORY OF AGRICULTURAL CHEMISTRY,  
UNIVERSITY OF WISCONSIN.

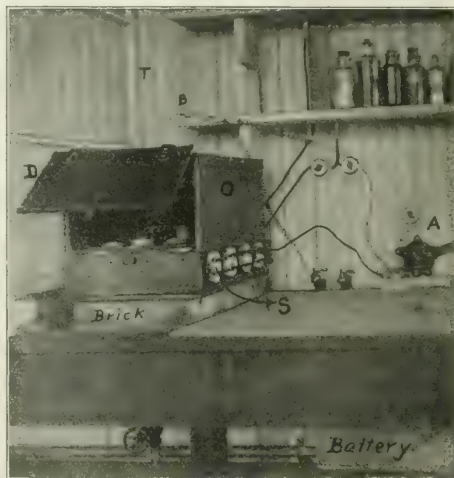
#### A CONVENIENT DRYING OVEN.

To some of the younger chemists in small laboratories, who have had trouble in finding a satisfactory drying oven for various temperatures, this device in use in our laboratory may have some suggestion.

We make no claims for originality in this device, and the ideas were suggested from various sources and concentrated in this oven. It consists of an oblong box "O" as shown in the cut  $12'' \times 12'' \times 18'' \times \frac{3}{8}''$  thick. The box itself is made of two thicknesses of thin black sheet-iron with  $\frac{1}{8}''$  transite asbestos board (obtained from H. W. Johns-Manville Co., of Detroit) between. All joints are bent and overlapped so that rivets or other fastenings are unnecessary. The oven is heated by electric lights in two circuits, one set being on continuously, and the other connected through a home-made thermostat device. The thermostat consists of a piece of fine capillary glass tubing (B) about 8" long, with a  $\frac{1}{8}''$  to  $\frac{3}{16}''$  thin bulb, blown on one end, and full of clean mercury. A small piece of platinum wire is sealed at this end, and another piece of wire is thrust in the other open end, to close the circuit as the mer-

cury expands. A consists of the magnet coils of an old worn-out electric bell. The soft iron bar of the bell was soldered to the end of a single knife switch, as short as possible, and four dry cells connected with the capillary tubing and coils, all in series. One set of lamps, put in staggered (all sockets on one side can be seen in cut), consists of four 16 candle power incandescent lamps continuously on, while the other set, for our use, three 16 candle power and one 32 candle power, is connected through the knife switch. The wire in the capillary tubing can be so adjusted that when the mercury expands to the desired temperature, the battery circuit will close, the magnet will attract the soft iron (that is, throw out the switch) and the other set of lights will go out. When the oven cools below the desired temperature, the mercury falls, the battery circuit breaks, and when the switch engages again (instantaneously), the lights go on.

Two 1" angle irons are fastened to the inner sides of the oven, forming a support for the oven shelf, which should be of thin iron and contain plenty of holes for circulation. The lamp sockets (S) extend through the oven and are made of porcelain. The door (D) is of same material as rest of the box, and is fastened with riveted hinges. Two 1" openings are left in top for



thermometer (T), thermostat (B) and vent. Care must be taken to have the knife switch as light as possible to work quickly without doing too much mechanical work to compromise accuracy of working, and the bore of capillary small enough to allow considerable expansion for each degree of temperature.

This makes a very satisfactory automatic oven, and will run very close to the desired temperature, depending on the skill in glass-blowing and adjustment of switch. A thermometer which we purchased specially constructed to cut off at 95° did not work as delicately as our own device. Any temperature may be obtained easily up to 150° C., depending on the number of watts consumed. We happen to use 95° C. with a maximum variation of about one degree each way. At 105° to 110° the variation is much smaller. The cost of the whole of this oven, including labor, was below \$10.00. The writer happens to know of no satisfactory automatic device similar to this on the market, and has seen none in the literature. There are no resistance coils to get out of order or burn out, and when the lights burn out it is only necessary to replace them by screwing new ones in the socket. Another, but not as satisfactory a

method is to have each light turn off and on separately and thus regulate the temperature according to radiation.

M. M. MACLEAN.

LABORATORY POSTUM CEREAL CO., LTD.,  
BATTLE CREEK, MICH.

#### DETERMINATION OF MERCURY IN THE MERCURY SALTS OF THE PHARMACOPOEIA.<sup>1</sup>

Nearly all of the mercury salts of the Pharmacopoeia are provided with standards of purity, known as Purity Rubrics; but none of them is correspondingly equipped with a quantitative method of analysis by which one may determine whether the salt is up to its required standard. The reasons for this state of affairs and the undesirability of such a condition will not be entered upon here. It is only desired at this time to call attention to quantitative methods of assay that have proved valuable in the examination of these chemicals and to recommend such methods for consideration by those interested. Some of the processes to be described here contain little that is new in the way of chemistry, but the application of them for pharmacopoeial testing may be new. Others of the processes may have a grain of new material in them.

If the mercury preparations of the U. S. P. are first converted into mercuric nitrate they are then readily subjected to electrolysis to determine the per cent. of mercury. This is practical with mercury oxide red, mercury oxide yellow, metallic mercury, and with mercury with chalk. Solution of mercuric nitrate U. S. P. may also be assayed for the mercury present after proper dilution to bring it to the usual concentration. The general statement of the method is to dissolve about 0.5 gram sample in about 1 cc. of nitric acid (sp. gr. 1.20), dilute to about 20 cc. and subject the solution to electrolysis. Use the mercury cathode and the rotating anode, the latter revolving about 700 to 800 times per minute. The voltage should be 10 to 12, the amperage 3, and 15 minutes at room temperature will be found sufficient time for the electrolysis to become complete. The mercury cathode is then washed with water, alcohol, and ether in the usual way, any increase in weight being due to the metallic mercury from the weighed sample with which the analysis began. Three-quarters of an hour or one hour easily covers the entire analysis from beginning to end.

In the case of mercury with chalk the mercury cathode and rotating anode have not been sufficiently tried, but with a stationary anode and a platinum dish as cathode the method is excellent. On account of the size of the cathode dish the sample is diluted to greater volume. It is well to weigh off a sample of about 1 gram, dissolve it in nitric acid, dilute to about 125 cc. and electrolyze aliquots of about 25 cc. each. Pass the current through the solution for two hours, keeping the temperature at about 70° C., the amperage about 0.05, and the voltage about 2. Wash the cathode dish in which the mercury is deposited in mirror-form (not in globules if done right) with water, alcohol, and ether as usual and weigh for increase in weight of cathode. The calcium present does not interfere with the electrolysis.

For ammoniated mercury, mercury iodide red, mercury iodide yellow, and mercurous chloride, a different procedure is advisable. These salts are all dissolved in solution of sodium sulphide and from this the mercury is deposited. The samples, about 0.3 to 0.5 gram, are weighed directly into the tared mercury cathode dish. 10 cc. of solution of sodium sulphide (sp. gr. 1.18) are added and a current of 0.5 to 0.75 ampere and 4 to 5 volts is passed for half an hour. Use the rotating anode running about 500 revolutions per minute. The mercury from the samples is deposited on that of the mercury cathode and all is washed and dried in the usual way with water, alcohol,

and ether. If any amalgam of sodium and mercury forms during the electrolysis allow the wash water to stand on it until it is all decomposed. The results are excellent.

Mercuric chloride is best treated in a simpler manner. To determine the mercury quickly in this place a sample of about 0.3 gram in a weighed mercury cathode dish, dissolve in 20 cc. of water, and, after adding a layer of about 10 cc. of toluene to protect the apparatus from chlorine gas, pass a current of about 1 ampere and 10 to 11 volts for fifteen minutes. The speed of the rotating anode to be used in this case is about 500 revolutions per minute. At the end of fifteen minutes the liquids may as usual be removed by decantation and the mercury cathode washed, dried and weighed. The method is accurate, and the time consumed by the entire analysis is about one-half to three-quarters of an hour.

It is perhaps advisable to add that in carrying out these tests no unusual dexterity or skill in manipulation is required, only a very elementary knowledge of electricity is needed, and the cost of the entire apparatus, exclusive of the platinum dish used in the one test, need not exceed thirty or thirty-five dollars. The work can therefore be carried on in any laboratory reasonably well equipped.

B. L. MURRAY.

#### THE OCCURRENCE OF SUCROSE IN GRAPES.

It has been positively stated by the most eminent writers on enology the sucrose does not occur in the fruit of grapes. For several of these statements consult the following:

Dr. J. W. L. Thudicum, "A Treatise on Wines," London, 1896, p. 65.

Babo und Mach, "Weinbau und Kellerwirtschaft," Berlin, 1896, Vol. 11, p. 2.

M. Victor Sebastian, "Traite Pratique de la Preparation des vins de Luxe," Montpellier, 1909, p. 84; and other statements of like tenor occur in the literature.

However, in 1908 Mr. H. C. Gore, of the Bureau of Chemistry, discovered sucrose in two varieties of Scuppernong grape, as in a communication to THIS JOURNAL.<sup>1</sup>

During the season of 1909 while conducting for the Bureau of Chemistry, the work on the chemical investigation of the grapes grown in the Lake Erie district, we found sucrose in several varieties of grapes belonging to the species commonly cultivated in the United States, but more especially in a new seedling grape discovered growing near Sandusky, O., which was until then unknown to horticultural literature.

The known varieties in which sucrose was found to occur are Hays, Pocklington and Worden. These showed sucrose in quantities varying from 4.49 grams to 5.66 grams per 100 cc. of juice. The new seedling, however, showed sucrose varying at different dates from 7.06 grams to 9.73 grams per 100 cc. of juice with a total sugar content varying from 15.93 grams to 19.52 grams per 100 cc. of juice.

While these determinations of sucrose on several cases have been checked by polariscope readings and are apparently correct, the full data will not be published until the whole subject can be re-examined the present season.

The occurrence of sucrose in large quantity in the fruit of grapes belonging to the types usually cultivated for wine and table use is so unexpected and important an observation that it is proper to exercise due caution before printing a detailed statement of the results. The purpose of this note is simply to record an interesting discovery.

However, it should not be presumed from the above statement that sucrose will probably be found in any considerable number of varieties of our common grapes. On the contrary, we have now examined in the laboratory a large series of samples of practically all the wine and table grapes grown in the Eastern States and in no case other than mentioned above have we

<sup>1</sup> Read at San Francisco Meeting, American Chemical Society, July 12-16, 1910

<sup>1</sup> 1, 436 (1909).



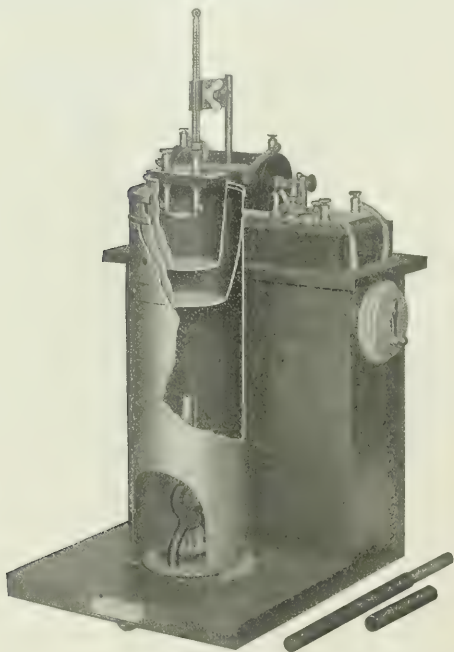
found sucrose in appreciable quantity. The analyses were made by Dr. B. G. Hartmann and Mr. John R. Eoff.

WM. B. ALWOOD.

STONEHENGE LABORATORIES, CHARLOTTESVILLE, VA.  
July 15, 1910.

### THE SCOTT OIL TESTER.

Scott's oil tester is a flash point apparatus for oils, varnishes, ether, alcohol, gasoline, turpentine, etc. While it has just made its appearance on the open market it has been in constant use for several years in the laboratory of its designer, Mr. D. G. Scott, of Chicago. It is electrically ignited and does away with the errors of personal equation, every determination being made under exactly the same conditions. One of the peculiar features of this apparatus lies in the electrodes which are so fashioned that when properly adjusted the spark travels backward and forward across a considerable portion of the surface of the oil so fast as to practically form a ribbon of fire about a quarter of an inch wide. The combustion or flash chamber



is so arranged that determinations may be made in freezing mixtures or high flash point determinations may be made over a naked flame. The amount of sample needed is exceedingly small, precluding danger from fire and thus making it particularly desirable for use in paint, oil and varnish laboratories.

The whole apparatus is self-contained, including batteries, etc., and occupies a space of only 8 by 10 inches on the table and is about 16 inches high. Its operation is very simple and its convenience apparent. It is durable and easily cleaned and its compactness and stability of design are such that it is as easily placed on the table ready for use or removed to the wall case for storage as a bottle or jar of the same size.

The first notice of this apparatus occurs in the new catalog of Messrs. E. H. Sargent & Co., of Chicago, who manufacture the instrument under the direction of Mr. Scott.

### CHROME PAINT ANALYSIS.

The chrome yellow paints on the market very frequently contain a number of constituents other than lead chromate, and the lack of any definite procedure in analytical works dealing with paints has led to the following attempt to arrive at a satisfactory scheme of analysis. A mixture containing the following ingredients was made:  $\text{BaSO}_4$ ,  $\text{SiO}_2$ ,  $\text{PbCrO}_4$ ,  $\text{PbO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{CaSO}_4$ , and  $\text{CaCO}_3$ . While it is not likely that all of these constituents would ever be present in a single paint, yet all of them have been found in chrome paints, and the following scheme of analysis can be applied to determine any or all of them.

(1) The silica and barium sulphate are separated by dissolving 1 g. of the paint in conc. HCl and evaporating to dryness twice with HCl. A few drops of HCl are then added and about 100 cc. hot water and the solution brought to a boil, allowed to settle, decanted through a filter and the process repeated. The insol. residue, which should then be white (if not a few drops of HCl are added and the process repeated until it is), is filtered off, washed with hot water several times and ignited in the blast in a platinum crucible and weighed. This gives  $\text{BaSO}_4$  and  $\text{SiO}_2$ . A few drops of  $\text{H}_2\text{SO}_4$  and some hydrofluoric acid are added and the  $\text{SiO}_2$  volatilized, and the  $\text{BaSO}_4$  weighed. The  $\text{SiO}_2$  is estimated by the loss in weight.

(2) The calcium present as sulphate is obtained from the filtrate from the  $\text{BaSO}_4$  and  $\text{SiO}_2$ . This is brought to a boil and the sulphate precipitated with  $\text{BaCl}_2$  in the usual manner. After settling, the  $\text{BaSO}_4$  is filtered off and washed thoroughly with very hot water (care must be exercised to wash out all the  $\text{PbCl}_2$ ), ignited and weighed. The  $\text{BaSO}_4$  is calculated to  $\text{CaSO}_4$ .

(3) The zinc oxide and calcium carbonate are obtained by treating 1 gram of sample with strong acetic acid, boiling, then diluting and filtering. The zinc oxide, all calcium salts and most of lead present as oxide pass into solution. The zinc and lead are precipitated with  $\text{H}_2\text{S}$  and filtered off, redissolved in hot dilute HCl and several grams of sodium acetate added; the lead is then precipitated as chromate by adding small excess of  $\text{K}_2\text{CrO}_4$ . This is filtered off and the zinc precipitated in the filtrate as carbonate by adding an excess of  $\text{Na}_2\text{CO}_3$  and digesting. The precipitate is filtered off, ignited and weighed as  $\text{ZnO}$ . The Ca which is in the filtrate from the Zn and Pb is precipitated as oxalate after making alkaline with  $\text{NH}_4\text{OH}$ , filtered, ignited and weighed as oxide. From total CaO is subtracted CaO present as  $\text{CaSO}_4$ , and the remainder calculated to  $\text{CaCO}_3$ .

(4) The ferric oxide is obtained by treating 1 g. of the paint with about 10 g. NaOH and 100 cc. water, heating to the boiling point, filtering and washing with hot water. The filter paper containing  $\text{Fe}_2\text{O}_3$ ,  $\text{BaSO}_4$ ,  $\text{SiO}_2$  and  $\text{PbO}$  is then ignited slowly in a porcelain crucible (to prevent its sticking to sides of crucible) and the residue digested with 5 cc. hot conc. HCl and transferred to a beaker with 50 cc. of water. The  $\text{BaSO}_4$  and  $\text{SiO}_2$  are filtered off and the filtrate almost neutralized with  $\text{NH}_4\text{OH}$  and the lead precipitated as sulphide and filtered off. The  $\text{H}_2\text{S}$  is boiled from the filtrate, the iron oxidized to ferric condition with a little  $\text{HNO}_3$ , precipitated with ammonia and weighed as  $\text{Fe}_2\text{O}_3$ . The filtrate from  $\text{Fe}_2\text{O}_3$ ,  $\text{BaSO}_4$ , etc., is used for the estimation of lead chromate. It is acidulated with acetic acid, when the insol.  $\text{PbCrO}_4$  is precipitated, filtered through Gooch crucible, dried on hot asbestos plate and weighed as  $\text{PbCrO}_4$ .

(5) To obtain  $\text{PbO}$ , 1 gram of paint is treated as for  $\text{BaSO}_4$  and  $\text{SiO}_2$ , the filtrate evaporated to dryness, taken up with a few drops of HCl, about 100 cc. hot water added and the solution boiled until clear green, adding more HCl if necessary. About 5-10 grams sodium acetate are then added to remove free hydrochloric acid. At this point the color of the solution

changes to reddish brown on account of the ferric acetate formed. A few cc. of acetic acid are now added and then 1 gram of potassium chromate, and the solution stirred vigorously. The lead is precipitated as chromate which is filtered off and washed thoroughly with cold water on a weighed Gooch crucible, dried on the asbestos plate and weighed. The weight of the  $PbCrO_4$  found in previous sample is subtracted from this and the difference is calculated to  $PbO$ . When white lead is present it is necessary to make a  $CO_2$  determination, and after deducting the  $CO_2$  due to  $CaCO_3$  the remainder is calculated to white lead and the excess of lead then figured as  $PbO$ .

The mixture analyzed had the composition shown in column 1 and the results obtained are given in column 2.

	1. Per cent.	2. Per cent.
$SiO_2$ .....	4.76	4.52
$BaSO_4$ .....	4.76	4.70
$Fe_2O_3$ .....	4.76	4.88
$CaSO_4$ .....	4.76	4.90
$ZnO$ .....	9.52	9.54
$CaCO_3$ .....	4.76	4.64
$PbCrO_4$ .....	57.14	57.04
$PbO$ .....	9.54	9.68
	100.00	99.90

E. F. SCHERUBEL.  
E. S. WOOD.

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## BOOK REVIEWS AND NOTICES.

**The Corrosion and Preservation of Iron and Steel.** By ALLERTON S. CUSHMAN and HENRY A. GARDNER. Large 8vo. pp. xv + 373. New York: McGraw-Hill Book Company, 1910. Price, \$4.00 net.

A book was needed which would bring together from the scattered literature the investigations and conclusions of the last few years on the corrosion and preservation of iron and steel. Although this work is still in progress and many investigators are engaged upon it, nevertheless it is high time that the conclusions reached thus far be presented in a single volume. This the authors have done in a way which is on the whole satisfactory and commendable. The development of the electrolytic theory of corrosion has been due largely to American workers, among whom the names of Whitney, Cushman and Walker stand pre-eminent, although others have contributed to no small degree. The development of the theory of corrosion is a triumph of which American chemists may well be proud. The first chapter, stating the problem of corrosion, is a satisfactory presentation of the question. Mention is made of the iron column of Kutab Minar at Delhi, India, supposed to have been erected 900 B. C., which has withstood atmospheric conditions for so many years without corrosion. A good deal of sentiment has been wasted on this column during recent years. It seems a pity that the Indian government has not investigated the physical and chemical properties of the column, or granted permission to somebody to do so. Chapter 2 takes up the Theory of Solution, and while it may be criticized on the ground that the statements are somewhat too absolute for dealing with a theory, the exposition is nevertheless good. Chapter 3 considers the Theory of Corrosion: discusses the carbonic acid theory, the peroxide theory, and finally the electrolytic theory. The development of the ferroxy indicator by Walker and Cushman and its application are given in detail. Chapter 4 deals with the Application of Electrolytic Theory; Chapter 5 is on The Inhibition and Stimulation of Corrosion; Chapter 6 is on The Technical Protection of Iron and Steel; Chapter 7, Relation of Pigments to the Corrosion of Iron; Chapter 8, Recent Field Tests on Protective Coatings for Iron and Steel; Chapter 9,

Paints for Various Purposes; Chapter 10, The Testing and Design of Protective Paints; Chapter 11, The Properties of Pigments; Chapter 12, The Properties of Paint Vehicles. This ends the body of the book. There is an appendix on The Corrosion of Water Jackets, and a bibliography of the subject reprinted from the bibliography issued by the Carnegie Library of Pittsburgh. The index covers 8 pages single column. The work is well printed and bound; the paper and illustrations excellent. All students of the subject will necessarily find the work desirable. It is a creditable addition to the literature.

**Soil Fertility and Permanent Agriculture.** By CYRIL G. HOPKINS. Cloth, 8vo. pp. xxiii + 653. Boston: Ginn & Company, 1910. Price, \$2.75.

Dr. Hopkins' name has appeared frequently in various recent scientific publications as an advocate of certain ideas in regard to soil fertility in opposition to those held by another school. It is, therefore, interesting to quote the first words in the introduction of the present book which appears to lay down Dr. Hopkins' fundamental doctrine: "It is the first business of every farmer to reduce the fertility of the soil, by removing the largest crops of which the soil is capable, but ultimate failure results for the land owner unless provision is made for restoring and maintaining productiveness. Every land owner should adopt for his land a system of farming that is permanent—a system under which the land becomes better rather than poorer." A little further along in the introduction, the author speaks so pointedly in regard to dealing with a technical subject, technically that his remarks are worth quoting for the benefit of writers in other lines of work: "In the preparation of this book free use has been made of such technical terms as are necessary to the discussion of fundamental principles with scientific correctness. No apology is offered for this. Farmers and agricultural students have at least as good intellects as other classes of people; and if when they leave the farm they can learn to understand and manage successfully such lines of business as banking, contracting, building, operating railroads, factories, and other commercial establishments—which they are doing everywhere—they can also understand their own business, if they will, when they remain on the farm or in control of land." This introduction is most interesting reading for the student, farmer or for the average man. The body of the book is divided into four parts and an appendix. Part 1, Science and Soil; Part 2, Systems of Permanent Agriculture; Part 3, Soil Investigations by Culture Experiments; Part 4, Various Fertility Factors. The book is evidently designed primarily as a text-book, and begins with the fundamentals of science and chemistry. The chemical part of the book is open to criticism on the ground that it is too artificial in its treatment. There is a tendency to make absolute statements where absolute statements cannot be made. It is too abstract, too academic, too much concerned with signs and symbols and too little with the realities of the science. "The bond between atoms may be likened to the hand clasp between persons, except that under normal conditions the hand of one atom always grasps the hand of another atom." (P. 4.) "The nitrogen atom has five bonds, or hands, but in some compounds only three bonds are used to hold other atoms. It might be conceived in this case that the other two hands are clasped together, and this conception might even be extended to cover a molecule composed of a single bivalent atom (such as mercury and, possibly, argon)." (P. 6.) In general it is doubtful if the use of fanciful similes in chemical theory has been of great benefit to the student or the science, certainly not now. The science of chemistry has been obscured by a jumble of bonds, hands, hooks, claws, oranges and peas, shot and cannon balls, smooth spheres and billiard balls until the

student has lost sight completely of the realities and becomes lost on a maze of obscure imagery. Pray let us reform this altogether! In the chapter on the earth's crust (in general good) there is some ground for remark. On page 48 the statements about gneiss are entirely misleading or untrue.

Dr. Hopkins is most at home in the chapters actually dealing with soil composition, surveys and analyses, sources of plant food, the uses of plant foods by plants, theory of soil fertility, the Rothamsted experiments and other field experiments. The chapters dealing with these subjects are in general excellent. They are, of course, colored by Dr. Hopkins' views on soil fertility, but he has nevertheless given a fair statement of the views held by his opponents, largely in the form of quotations. Naturally a considerable portion of the book is devoted to discussion of the Rothamsted experiments; a smaller portion to Ohio, Illinois, Minnesota, Canadian and other field experiments. Under Various Fertility Factors he discusses Manufacture of Commercial Fertilizers, Crop Stimulants and Protective Agents, Critical Periods in Plant Life, Farm Manure, Losses of Plant Food from Plants, Losses of Plant Foods from Soils, Analyzing and Testing Soils, Relation of Fertility to Appearance of Soils or Crops, Factors in Crop Production, Essential Factors of Success in Farming, The Value of Land, and Two Periods of Agricultural History. The last chapter mentioned consists of quotations from the ancient Roman writers down to Abraham Lincoln and Daniel Webster on the subject of fertility of the soil. The appendix consists mainly of statistics and tables of analyses of soils. There is a good index. The book is well printed and bound, and illustrated principally by reproductions from photographs of well-known agricultural chemists and directors of experiment stations.

There is a two-page map of the United States and one of Illinois showing the soil provinces, which are examples of good printing. The book is a welcome addition to the literature of the subject and barring a few features of the chemical and geological chapters the presentation is excellent.

**The Chemists' Pocket Manual.** By RICHARD K. MEADE. Second Edition. Black flexible leather.  $4 \times 6\frac{1}{2}$  inches. pp. xii + 443. Easton: The Chemical Publishing Co. 1910. Price, \$3.00 net.

This little book is really a chemists' pocket book. It might also be called a chemical engineers' pocket book on account of its inclusion of much engineering data seldom inserted in chemical books of this sort. Since the first edition was issued several years ago much material has accumulated and the present volume appears to be of about double the contents of the former. The book is subdivided by the following headings which give a good idea of its plan and makeup: Metric and United States Weights and Measures; Mathematical; Mensuration, International Atomic Weights, 1908; Stoichiometry; Graphic Methods for Saving Calculation; Conversion Tables; Specific Gravities of Solids and Liquids; Weight and Volume of Substances; Standard Tables of Specific Gravity of Sulphuric Acid, Nitric Acid, Hydrochloric Acid and Ammonia, Adopted by the Manufacturing Chemists' Association of the United States; Lunge's and Other Tables of the Specific Gravity of Acids and Alkalies; Physical Properties of Gases; Hygrometers; Solubility; Boiling-Point and Melting-Point; Standardizing Weights; Calibration of Chemical Glassware; Temperature; Heat; Combustion; Radiation; Electricity; Mechanics; Mineralogy; Determinative Mineralogy; Geology; Volumetric Solutions; Standardizing Volumetric Solutions; Reagents Used in Quantitative, Qualitative and Gas Analysis; Indicators for Volumetric Analysis; Test Papers; Special Reagents; Solutions for Gas Analysis; Miscellaneous; Scheme for the Qualitative Analysis of a Substance; Assaying; Analysis of Iron Ores; Determination of Copper in Ores, Mattes, Etc.; Determination of Lead in Lead Ores; Determination of Zinc in Zinc Ores; Determination of Sulphur in Lead, Copper and Zinc Ores; Analysis of Iron and Steel;

Analysis of Blast-Furnace Slags; Analysis of Alloys of Tin, Antimony, Lead, Copper and Zinc (Bearing Metals); The Analysis of Coal; Analysis of Fuel Gases; Analysis of Blast-Furnace Gas, Illuminating Gas, Producer Gas, Etc.; Determination of the Hardness of Water; Complete Examination of Water for Boiler Purposes; Rapid Analysis of Water for Boiler Purposes; The Examination of Potable Water; Chemical and Physical Examination of Portland Cement; Analysis of Limestone, Cement Rock, Lime, Rosinade Cement, Etc.; Analysis of Clay, Fire-Clay, Fire-Brick, Etc.; Examination of Lubricating Oils; The Analysis of Soap; Chemical Analysis of Mixed Paints; The Chemical Analysis of Mixed White Pigments; The Analysis of Fertilizers; Determination of Carbon and Hydrogen in Organic Substances; Determination of Nitrogen; Index.

The binding and print are good and the paper, which at first appears somewhat thick, is found to be tough and of good wearing quality—most desirable in a work of this sort. The book will find many users among works chemists, who want just the sort of information covered in a single compact volume.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### AMERICAN ELECTROCHEMICAL SOCIETY.

Chicago Meeting, October 13-15, 1910.

The eighteenth general meeting of the American Electrochemical Society, which was held in Chicago October 13, 14 and 15, 1910, was a splendid success. The registration showed a total enrolment of about 230 members and guests present at the meeting. The arrangements of the local committee and the officers of the Society were complete and well perfected, so that each event took place according to schedule and to the complete satisfaction of those in attendance at the meeting.

The first session was called to order by President William H. Walker, of Boston, at 10.00 A.M., October 13th, in the Florentine room of the Congress Hotel. The program of papers has already been published in these columns.<sup>1</sup> The papers of greatest interest to our membership will be published in *THIS JOURNAL*. Dr. E. Weintraub's paper on cast copper (not on the printed program), read by Mr. A. B. Marvin, of Chicago, on account of Dr. Weintraub's absence, excited great enthusiasm. Samples of cast copper made by the process were exhibited to the Society. Dr. Richards read a paper on the Hiorf electric furnace, also not on the printed program. A third paper, not previously announced, was by Mr. F. T. Snyder, entitled "The Flow of Heat through Furnace Walls."

In the afternoon there were several excursions, largely participated in. The evening was left free and was utilized by the members mainly for promoting acquaintanceship and good feeling.

On Friday morning, October 14th, the reading of papers was resumed in the Florentine room at 9.00 A.M. One of the most pleasing and vital features, characteristic of all the sessions was the general discussion of papers heartily entered into by the audience.

On Friday afternoon there were excursions to the plants of the Illinois Steel Co. at South Chicago, the Indiana Steel Co. at Gary, Ind., and Sears, Roebuck & Co.

#### ILLINOIS STEEL CO.

At the Illinois Steel Co.'s plant the party witnessed the operation of the 15-ton Héroult electric steel furnace, which is working on blown metal from the Bessemer converters. This furnace has been in operation over seventeen months. Its electrical equipment consists of three 750 kw. transformers to reduce the three-phase twenty-five cycle power from 2200 volts to approximately 90 volts, so as to obtain approximately 50 volts at each arc. This trip was made particularly interesting by the presence of Dr. Héroult. After the electric furnace,

<sup>1</sup> See *THIS JOURNAL*, October, 1910.



other parts of the plant were visited. While the Gary plant in time is destined to be the largest plant in the world, the South Chicago plant has up to the present time held its own remarkably well. No single thing shows the development of the plant better than the increase in the use of electrical power during recent years. Twelve years ago the electrical power generating equipment consisted of a 400 kilowatt unit. Six years later this had been replaced by a 3000 kw. plant. Then followed rapidly one increase after another until now three power generating stations are in operation with a total capacity, including that under construction, of 33,000 kw., the same comprehending steam engine driven, gas engine driven and high-pressure and low-pressure turbine driven, units varying in size from 400 kw. to 7000 kw. Several sub-stations for transforming the energy to lower voltage are in service; likewise numerous local transformer stations. Plans under discussion will no doubt result in more than doubling the present capacity within two or three years.

The electrical energy is utilized for every conceivable purpose in every department of the plant. A few years ago problems were solved by means of hydraulic or steam power. One need not enter one of the newer mills to perceive the absence of such power. An application of electrical power is invariably resorted to in solving mill problems.

The generating stations of this plant supply power for 2000 motors, aggregating 90,000 h. p., an electric reducing furnace requiring 1500 kw., and the necessary plant illumination. A rail mill for rolling light sections has two 2000 h. p. motors on the main rolls. A universal plate mill has a 6000 h. p. motor on the rolls. A new structural mill will have 4000 h. p. on the main rolls. From such sizes down to fan motors are found in this plant.

At the Gary plant the visitors were shown the facilities for handling ore, the blast furnaces, gas washers, power plants and mills.

On Friday night the banquet was attended by 85 members and guests.

Saturday morning the reading of papers was continued in Kent laboratory, at the University of Chicago. Among others, Prof. Milliken spoke on the "Isolation of an Ion and the Precision Measurement of Its Charge," detailing his recent fundamental researches in this field. Prof. Milliken's personality, as well as his subject matter, aroused the greatest interest and enthusiasm in his listeners.

Luncheon was served at the University Commons.

#### CHICAGO DRAINAGE CANAL AND POWER PLANT.

In the afternoon the Society left by special train for Lockport to inspect the Sanitary and Ship Canal and Power Plant of

the Chicago Sanitary District at that place. The combination of sewage disposal canal, ship canal, and electric power plant is unique and the visitors were delighted with the splendid engineering achievement.

This excursion was the last feature of the program and the visiting members, for the most part, left Saturday night for their homes.

#### TAYLOR INSTRUMENT COMPANY'S EXHIBIT.

One of the interesting features of the meeting was the pyrometer exhibit of the Taylor Instrument Company, arranged near the meeting place. They classify their instruments into three groups:

1. Radiation Pyrometers.
2. Resistance Pyrometers.
3. Thermo-couple Pyrometers.

The application of these various instruments depends chiefly on the temperature they are to measure and for convenience we will describe their limits as follows:

Class 1. For temperatures of 1500° F. and upward.

Class 2. For temperatures from the lowest to 2200° F.

Class 3. For temperatures up to 2500° F.

The most satisfactory form of radiation pyrometer is one so constructed that error in bringing the object under observa-



Thermo couple.

tion is impossible. It must not depend upon color, as it is a well-known fact that one and the same hue will not appear identical to two observers.

The Fery radiation pyrometer overcomes this objection by having a mechanical focusing device which insures proper observation and is entirely independent of color comparison. The instrument is virtually a reflecting telescope with the hot junction of a sensitive thermo-couple at the focus of the concave reflecting mirror. The radiant heat emanating from a body is collected by the mirror and focused upon the couple generating electrical energy of sufficient magnitude to be measured on a millivolt meter. As the thermo-couple has both its hot and cold junctions very close together, the instrument is practically independent of surrounding temperature. Furthermore, within wide limits it is unaffected by the distance at which it works. It may be used as an indicating instrument and the complement of the outfit in this case comprises the telescope, cable, tripod and indicator with two scales, viz., 1000° F. to 2400° F. and 1600° F. to 3600° F., or their centigrade equivalents, or if records of temperature are desirable the thread recorder is supplied. This instrument is a highly sensitive galvanometer entire free of friction. It gives a record with rectangular coordinates. As the record is written in ink it is permanent and requires no further fixing.

The resistance thermometer consists of a mica frame upon which is wound fine platinum wire. This "bulb" is about 3 to 4 inches in length and the fine wire is connected to stouter wire at its upper extremities. If the temperatures under con-



Chicago Sanitary District Power House at Lockport, Ill.

sideration are high, these lead wires are platinum; for lower temperatures, however, they are usually copper. The lead wire and bulb are protected by a suitable covering sheath. As the bulb becomes heated its electrical conductivity is lessened, while conversely the lower its temperature the less resistance it offers to the flow of current.

Measurements of resistance can be made very accurately on the Wheatstone bridge, hence by applying this principle in the construction of the Whipple indicator and suitably calibrating the resistance scale to read directly in temperature units, an instrument of extreme precision is obtained. As a balanced method is used, two additional wires (making 4 in

operate on a battery circuit they may be used in isolated places where no source of electrical supply is available.

This method of temperature measurement is the most accurate as yet devised.

The Thermo-electric Thermometer or Thermo-couple is one of the most convenient forms of apparatus for measuring temperatures. Its bulk is small, and it can be made up in various shapes to suit widely different conditions.

The Platinum, Platinum-Rhodium Couple is capable of use for temperatures up to 2500° F. and even higher, the alloy is stable and deterioration in use very slow. The melting points of the two component metals are very high, over 3000° F., and the wires are strong and tough. If, after long use, the electromotive force of a couple has fallen, it can be almost completely restored to its original value by electrically annealing the wires in air at a bright yellow heat.

The actual electromotive force measured is the difference between that of the two junctions of the couple; for accurate work it is therefore important to keep the so-called cold, or comparison, junction at or near a constant known temperature.

For high temperature measurements in industrial work it is usually sufficient if the comparison junction in the thermo-couple head is kept fairly cool in the air outside the furnace, and this consideration frequently decides the length of the couple.

As with the Féry pyrometer, the thermo-couple may be used with either indicator for instantaneous value of temperature or with the thread recorder where continuous records are desired.



Whipple indicator.

all) are led from the thermometer. This affords a means of comparison so that the correct operation of a thermometer is assured regardless of the distance from the Whipple indicator, hence the suitability for temperature measurements of most inaccessible locations as mines, water tanks, chill rooms, hot blast mains, etc.

A Callender Recorder is used for obtaining continuous records of temperature. This instrument also embodies The Wheatstone Bridge principle and is exceedingly rapid in following the slightest changes of temperature. A very open rectangular scale is therefore provided.

As both the Whipple Indicator and Callender Recorder

## THE AMERICAN IRON AND STEEL INSTITUTE.

New York Conference, October 14 to 22, 1910.

Friday, October 14th, 10.30 A.M., Myrtle Room, Waldorf Astoria Hotel.—Reading and discussion of papers. Address by the President, E. H. Gary. "Foreign Relations," by James A. Farrell. "Betterment of Labor Conditions," by William B. Dickson. "Contract Obligations," by Willis L. King. "The International Metallurgical Congress at Düsseldorf," by Charles Kirchhoff.

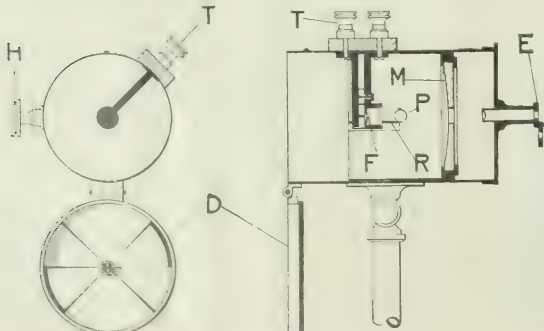
7.30 P.M.—Banquet in the Astor Gallery.

October 15th to 22nd.—Special excursion to inspect the large steel industries of the country, Buffalo, Gary, Chicago, Pullman, Pittsburg and Washington being included in the itinerary.

The recent meeting in New York of the American Iron and Steel Institute and the subsequent tour through the country, inspecting the great steel centers, is unique. There have been several previous tours in this country of representatives of the large iron and steel industries, notably those of 1890 and 1904, at the invitation of the American Institute of Mining Engineers, but never before in this country or in Europe has an international meeting been gathered together, the primary import of which is to discuss the commercial aspect of domestic and international relationship.

Two years ago, Chairman Gary, of the United States Steel Corporation, was tendered a dinner in London by the officers of the Iron and Steel Institute of Great Britain. At that dinner Judge Gary outlined a certain policy which he thought could be adopted to the greatest economic advantage by the great steel industries. In his own words this doctrine was "competition, but not hostility; rivalry, but not antagonism; progress and success for all, but not the punishment or destruction of any." And this meeting in New York may be taken as a direct furtherance of this policy.

Thirty foreign representatives, including some of the most important masters of the iron and steel manufacturers of Great Britain and Europe, attended this meeting as the guests of the Institute.



Féry pyrometer.

The first day, Friday, October 14th, was given up to the reading and discussion of papers, the very nature of which indicates the general purport of the whole meeting.

"Foreign Relations," "The Betterment of Labor Conditions," and "Contract Obligations" suggest that this meeting is not a mere metallurgical conference but rather a desire for a better international understanding, a binding together of foreign sympathies and the wish for more complete co-operation in the handling of the great problems of international trade and competition.

And then, too, after the formal meeting and the opening dinner in New York, the subsequent tour through the country with its attendant inspection of the leading industrial centers was but another step toward the same end.

By special train and special arrangement, handled by committees composed of representatives of the leading commercial interests in each great city to be visited, about seventy-five members and guests visited the following centers in turn. Leaving New York Sunday evening, the party proceeded to Buffalo. Here the plant of the Lackawanna Steel Company was visited and later the Mammoth Lock at Black Rock was seen. From Black Rock the party went to Niagara Falls, where several hours were spent in a tour of the gorge and a visitation of several of the power plants.

From Niagara Falls the party left for Gary, Indiana, where Tuesday morning was spent in a tour through the wonderful new plant of the Illinois Steel Company.

On Tuesday afternoon the party inspected the South Works of the Illinois Steel Company, and in particular the Héroult Electric Furnace and the Gayley Dry Blast.

Tuesday evening a brilliant dinner was held at the Blackstone Hotel, with President Gary in the chair.

Wednesday was occupied in visits to the plants of the International Harvester Company, the Pullman Company, and the stock-yards.

Thursday, at Pittsburg, was spent in a steamboat trip up the Monongahela River to view in outline the great mills clustered on its banks. The Jones & Laughlin and the Carnegie Steel Company plants were visited, and in particular the Homestead Works.

Friday morning was devoted to an inspection of the Carnegie Institute, and the afternoon to a visit to the Westinghouse interests in East Pittsburg.

Finally the tour was brought to a fitting conclusion by a visit to Washington and a reception tendered the Institute and its guests by President Taft.

The importance of a great conference of this kind cannot be overestimated. Not only are the leading manufacturers of this country brought into closer and more intimate relationship with those of Great Britain and Europe but an understanding of local conditions, an appreciation of local sympathies, and an insight into the magnitude of our steel industries are obtained from a trip of this kind that can be obtained in no other way.

The United States for some time has been the leading manufacturer of iron and steel products, and the need for some such body as the Iron and Steel Institute has long been felt. The technical side of this great industry has been adequately dealt with by the Institute of Mining Engineers, the Society of Mechanical Engineers, the Chemical, Electrochemical and similar societies, but the commercial aspect and the executive aspect has been, till now, somewhat neglected.

The commercial and business aspects of the iron and steel industry have just as much need for discussion by the executives of the great companies as have the technical points by its engineers and scientists. And it is this aspect of the iron and steel industry that the American Iron and Steel Institute will embrace, in addition to bringing together the work of the scientists and technical societies.

CHAS. GLIDDEN OSBORNE.

## AMERICAN LEATHER CHEMISTS' ASSOCIATION.

The Seventh Annual Meeting, Chicago, 1910.

The seventh annual meeting of the American Leather Chemists' Association was held in conjunction with the convention of the National Association of Tanners at the Hotel La Salle, Chicago, Ill., October 6th, 7th and 8th, convening at 9.30 o'clock, A.M., Thursday, the 6th. The program was as follows:

Thursday, October 6th, Morning Session.—Opening remarks by the president. Report of the Secretary-Treasurer. Committee reports.

Afternoon Session.—Address by Dr. Allen Rogers, "Trade School for the Leather Industry." Address by Mr. George A. Kerr, "Manufacture of Extracts in the United States." Address by Mr. F. C. Rose, "Leather Oils." Address by Mr. John H. Yocum, "Disinfection of Hides."

Friday, October 7th, Morning Session.—Meeting of the National Association of Tanners. Members of the A. L. C. A. are invited to attend this meeting.

Afternoon Session.—Visit to the stock-yards: Armour & Co., Swift & Co., Libby, McNeil & Libby.

Evening.—Joint banquet at the Hotel La Salle. The National Association of Tanners have cordially invited the active members of the A. L. C. A. to attend this banquet as their guests.

Saturday, October 8th, Morning Session.—Address by Mr. F. P. Veitch, subject to be announced. Address by Mr. F. E. Atteaux, "The Proper Bating of Hides." Address by Mr. J. H. Russell, "Tannage of Heavy Leather in California." Address by Mr. George A. Riker, "Extraction of Leather by Various Solvents."

Afternoon Session.—Address by Mr. Thomas A. Faust, "The Necessity of Proper Sampling." Address by Mr. R. C. Jacobsen, subject to be announced. Committee reports. Election of officers.

H. C. REED,

Secretary.

## AMERICAN CHEMICAL SOCIETY.

Joint Meeting, Cincinnati, Nov. 12, 1910.

The Cincinnati Section of the American Chemical Society will hold a joint meeting with all the neighboring Sections on November 12th, in Cincinnati.

Dr. W. D. Bancroft, President of the National Society, has been secured as the main speaker, and his subject will be "The Measurement of High Temperatures in the Electric Furnace."

An honorary banquet will be given by the local section to all the visiting members of the American Chemical Society and side trips have been arranged to all points of interest in our city.

Guides will be appointed to escort the visitors to any industrial plant or section of the city that they wish to go to, and will see that all the wishes of the visitors are gratified.

ALFRED SMITH, Secretary.

October 7, 1910,  
RING PLACE, PRICE HILL,  
CINCINNATI, OHIO.

## PERSONAL NOTES.

Dr. Charles A. Crampton, for many years chief chemist in the U. S. Govt. Internal Revenue Service, has established a commercial laboratory in the Evans Building in Washington, D. C., and left the government service.

Mr. Robert E. Divine, analytical and consulting chemist of Detroit, Mich., has moved from the Park Building into more commodious quarters at 138 Monroe Ave.



Dr. Heinrich Caro, industrial chemist and recently director of the Badische Anilin- und Soda-Fabrik, died on a journey to Dresden on Sept. 11, 1910, at the age of 76 years.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**969,253. Process for Recovering Metal.** ARCHIBALD W. DIACE, of Detroit, Michigan, Patented Sept. 6, 1910.

This invention comprises a process for recovering metals from the skimmings, and other dross, and for melting down borings and other small particles and pieces of such metals as readily oxidize when heated.

While this process is not necessarily carried out by any particular type of mechanism, that shown in the accompanying illustration embodies features necessary to the carrying out of this process. An oil, gas, or solid fuel furnace, 1, of well-known construction, contains the crucible 2 and is closed by

Above the furnace is mounted a hopper, 10, having a spout, 11, connecting with the pipe 12, which pipe connects to the tube 7 in any desirable manner, a connecting sleeve, 13, being shown. At the upper end of the pipe 12 may be mounted a frame, 9, in which are revoluble the shaft 14 and a tube, 15. On the shaft 14 may be secured a pulley, 16, and a pinion, 17, which latter meshes with the gear 18 on the tube 15. A screw-conveyer, 19, is secured to the tube 15 and will be turned by the shaft 14. The parts above the furnace top 3 may all be of cast iron, and any other mechanism may be employed to force the material down the tube 7. Arrangements may also be made for preheating the material in its passage from the hopper to the molten metal in the crucible.

Dross such as skimmings, from melted aluminum and of light-weight alloys, contain large amounts of metal. When such dross is packed into a crucible and heated to the melting point of the metal or alloy, the oxides and other impurities do not separate readily, as their specific gravity is so nearly that of the metal or alloy. In view of the fact that these metals readily oxidize at the melting point, much not already an oxid becomes so during this heating.

By thrusting the mingled metals, oxid and other impurities below the surface of a heavier metal with which it readily forms an alloy, the oxid is released, and, because of the great difference in specific gravity, immediately rises to the surface, covering the same and retarding further oxidation.

When the apparatus used in the drawing is employed, the mixed oxid and metals are thrown into the hopper 10, and slip down to the pipe 12 through the spout 11. The screw 19 slowly feeds down this material at a constant speed, forcing it down into the molten mass which fills the lower end of the tube 7. By the time the material is forced out of the lower end of the tube, the metal will have been melted and absorbed by the molten mass in the crucible and the oxid will float to the surface, 21, of the mass. As more metal is added to the amount already in the crucible, and the surface rises, the oxid will come near to the opening 6, where it can be skimmed off.

This process may be modified to recover the metal of borings and scraps of such metals as readily oxidize near the melting point. A quantity of the metal is first melted, after which the borings and scraps are forced down into the molten mass through the tube 7. This tube prevents the oxidizing flame reaching the finely divided metal, which really does not melt until under the surface of the main mass. The tube 7, or its equivalent, can be filled with an unoxidizing or neutral atmosphere so as to further protect the metal.

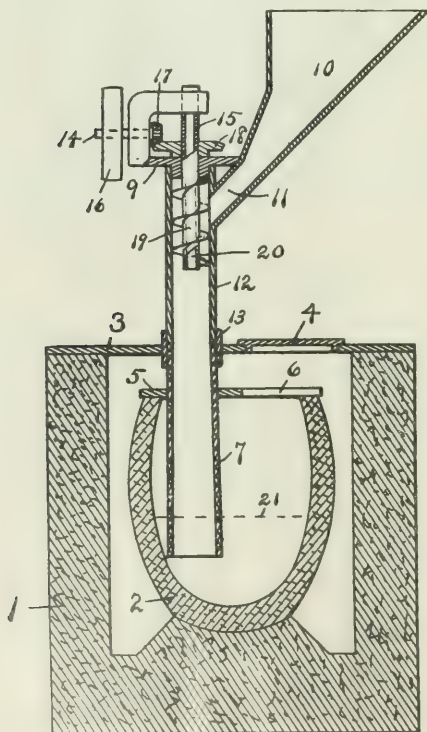
It is sometimes desirable to mix a proper flux, such as ammonium chlorid, with the mixed metal and oxides and with the metal borings before submerging the same in the molten metal.

**969,773. Process of Producing Alloys and the Separation of Metals.** PERCY F. COWING, of New York, N. Y., Sept. 13, 1910.

This process relates to the electrolytic treatment of alloys containing principally copper and nickel, and in certain cases iron, the object being to separate the copper and to recover nickel and iron economically and by simple operations. The nickel and iron are obtained in the form of a compact thick deposit on the cathode.

In carrying out the process the original alloy is placed as an anode in an electrolytic bath, which, upon the passage of the current, has the property of dissolving substantially all of the metals of the original alloy. That portion of the electrolyte forming the resultant solution is then treated in such manner as to replace the copper by iron, or nickel and iron, and nickel and iron are thereafter electrolytically deposited.

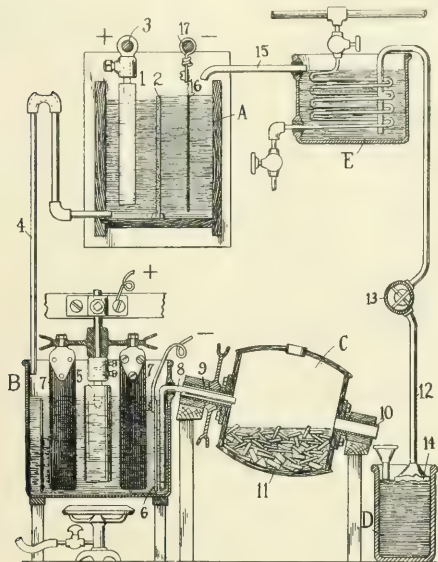
A warm, rather concentrated, substantially neutral aqueous



the cover 3, having an opening closed by the lid 4. A top, 5, partly covers the crucible and has an opening, 6, through which access is had to the contents. A refractory tube, 7, unacted upon at the temperature employed, preferably of carbon, extends down into the crucible below the line of the molten contents.

solution of nickel chlorid is a suitable initial electrolyte for carrying out the process. The very soluble nickel chlorid dissolved in water forms, especially when hot, an electrolyte of low electrical resistance and permits the use of high current densities.

The first vat, A, comprises an anode compartment and a cathode compartment, wherein the copper-bearing alloy 1 to be treated is dissolved as the anode, and nickel and iron are deposited on the cathode. The anode and cathode compartments are separated by a diaphragm, 2. The rest of the apparatus is for modifying the copper-containing solution which is withdrawn from the anode compartment of this vat, A, and for discharging it, after proper treatment for the removal of the copper therefrom, into the cathode compartment thereof. The anode and cathode and the electrolytes in the two compartments of this vat constitute a divided electrolytic cell in which the alloy to be treated is dissolved and the desired metal or metals obtained. The dividing diaphragm of the vat is of that type which is sufficiently non-porous to prevent



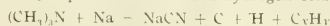
the mixing of the solutions on either side thereof to any appreciable degree, but at the same time has sufficient porosity to allow the electric current to be conducted therethrough by the electrolyte in its pores without too greatly increasing the resistance. The original alloy is connected as the anode to a positive bus-bar 3. When the electric current is passing, the original alloy goes into solution in the electrolyte in the anode compartment of the vat A. The solution thus formed is carried from the bottom of this compartment through a conduit, 4, into a second electrolytic vat, B, in which selective deposition is carried on. The anode 5 in this vat is composed of nickel or iron or both, and the cathode 6 may be composed of copper; but this is not essential. The electrolyte is preferably agitated by stirrers, 7, and may be heated. By maintaining a sufficiently low impressed voltage between the anode and cathode, the copper-containing solution from the anode compartment of the first vat A in its passage through the second vat, B, is caused to deposit copper selectively upon the cathode, 6, an equivalent amount of the anode 5 going into

solution to replace the copper. It is not expected that all of the copper in the solution be so replaced. It is obvious that a series of vats for selective deposition of copper may be used. The solution is withdrawn from the vat for selective deposition, or from the last of these vats if more than one is used, through a conduit, 8, which communicates with the interior of a receptacle or series of receptacles, C, wherein the copper still remaining in solution is removed by cementation on iron. It is here shown as a tumbling barrel mounted on an inclined axis by means of hollow trunnions, 9 and 10, the conduit entering through the upper trunnion. This tumbling barrel contains loose pieces or fragments of iron, 11, which it is desired to substitute for the copper remaining in solution after leaving the selective deposition vat. While the substitution is herein being effected by cementation, the tumbling action is of advantage, as it dislodges some of the cemented copper from the iron fragments in the receptacle and prevents their adherence to each other and, by agitation, continually brings fresh solution into contact with the fragments. As already indicated, a series of these cementation receptacles may be used. Sufficient time is allowed during the passage of the solution through the vat for selective deposition, B, and the cementation receptacle C to permit the replacement of the copper. When this replacement has taken place sufficiently, the solution is discharged from the cementation receptacle, or the last of these if more than one is used, through the lower trunnion into a settling tank, D, in which any undissolved material carried over mechanically is allowed to settle. The solution now freed from the salts of copper, and containing the salts of iron, or iron and nickel, substituted therefore, is conveyed from the settling tank to a heating tank, E, through a conduit, 12, by any suitable means, a pump, 13, being illustrated. A filter, 14, can be introduced between the settling tank and the heating tank, if desired. This solution is then conveyed through a conduit, 15, from the heating tank to the cathode compartment of the first vat A, the temperature of the solution being raised to a sufficient degree in the heating tank or in the vat A to maintain in the cathode compartment that temperature of the electrolyte at which the electrolytic process is most efficiently carried on. The bath in this cathode compartment contains nickel and iron in solution. A cathode, 16, is immersed therein upon which metals are deposited from the solution. This cathode is suspended from a negative bus-bar, 17. When the desired amount of metal has been deposited upon the cathode, the cathode is removed. The solution in the cathode compartment is allowed to flow over the diaphragm 2 into the anode compartment, thereby completing the circuit flow. The deposit or the cathode and deposit constitute the produce which my process is designed to secure. By depositing predetermined weights of nickel, or nickel and iron, upon a cathode of known weight and material, as iron, the relative weights of these metals in the cathode and its deposit may be varied as desired.

969,885. Process of Making Sodium Cyanid. OTTO LIEBKNECHT, of Frankfort-on-the-Main, Germany. Assignor to the Roessler & Hasslacher Chemical Co., of New York. Patented Sept. 13, 1910.

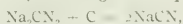
This invention relates to a process of making sodium cyanid from metallic sodium by reaction with trimethylamin.

The patentee has discovered that if dry vapors of trimethylamin are passed into highly heated molten metallic sodium the formation of sodium cyanide takes place in connection with the formation of various carbon-hydrogen compounds, carbon and hydrogen, as may be illustrated by the following equation, in which  $C_xH_y$  represents the carbon-hydrogen compounds:

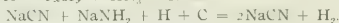
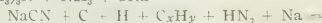


The sodium cyanid may subsequently be freed from the

carbon by any of the usual mechanical means as, for instance, by filtering the mixture, the carbon-hydrogen compounds and the carbon-hydrogen compounds passing off at the high temperature used, as gases. The formation of carbon in this free state may also be avoided chemically, for example, by the addition of disodium of cyanamid which combines with the carbon to form sodium cyanid, according to the equation



disodium cyanamid being added until a sample does not show any more carbon; or ammonia may be added to the trimethylamin whereby a separation of carbon is prevented, in accordance with the following equations:



The formula  $\text{C}_2\text{H}_2$ , as before stated, represents the carbon-hydrogen compounds which at the high temperature used exist in gaseous form and pass off as a gas, together with the hydrogen.

The accompanying illustration shows diagrammatically a form of apparatus with which the process may be practiced.

In the drawing, A represents a pot, preferably of iron, set in a suitable furnace.

B is a burner for heating the furnace and pot and may be of any suitable construction, preferably in the form of a gas burner.

The pot A is provided with a cover, C, in which are suitable

Intake pipe D is provided with a cock, E, and exhaust pipe H is provided with a cock, J. Connecting with the exhaust pipe H is a pressure pipe, K, controlled by a cock, L, and leading to any suitable source of pressure.

In practicing, the process in connection with apparatus of the above type, 7 kilograms of sodium may be heated in pot A to about 700° Centigrade, the temperature being determined by a thermometer inserted in thermometer pipe F, and about 18 kilograms of trimethylamin passed in through intake pipe D. Cock L should be closed and cock J opened so that the waste gases may pass off through exhaust pipe H. When the reaction is finished and sodium cyanid formed the cocks E and J are closed, cock L opened and pressure applied through pipe K, which forces the finished charge up through pipe G to a suitable filter. The sodium cyanid formed, as stated, contains free carbon, which may be removed by filtration or otherwise, as stated above, so that the resulting sodium cyanid will be white.

969,907. Method of Recovering Ammonia from Coal-Gases and the Like. JAN ADOLF ROELOFSEN, of Middlesbrough, England. Assignor to the Actiengesellschaft Fuer Kohlen-destillation, of Düsseldorf, Germany. Patented Sept. 13, 1910.

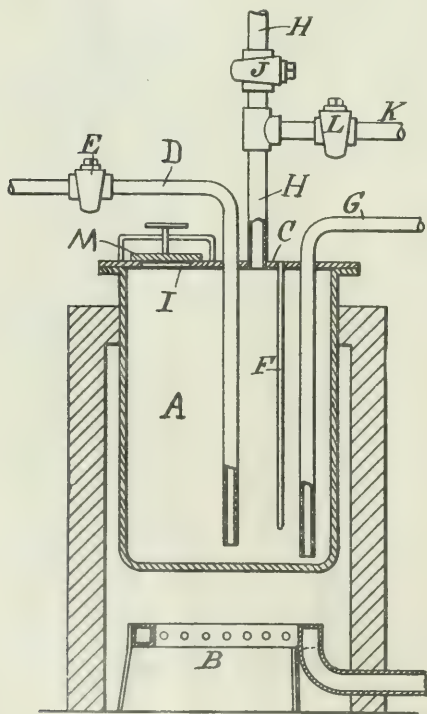
The object of this invention is to recover ammonia from gases as a salt, preferably sulfate, by means of a smaller and more economical installation than in the prior processes, and without the reheating of the gases of carbonization which, if these gases are subsequently treated for the extraction of benzol, require to be cooled afterward; further, to prevent the contamination of the marketable ammonium salts by tar and the like, and the contamination of the gases of carbonization, from which the tar and ammonia have been separated, by obnoxious gaseous ingredients, which render these gases inapplicable for illuminating or power purposes, and lower their calorific value unless purified by expensive processes.

A further object is to greatly reduce the amount of obnoxious effluent produced and, finally, to effect economies by using hot air, hot products of combustion, or other hot neutral gases, which do not permanently combine with ammonia, in place of steam, in the operation of the ammonia still, and to maintain the concentration of the acid solution of the ammonium salts by superheating the vapor obtained from the ammonia still before they enter the acid solution.

The gases of carbonization, coming from coke ovens, retorts or the like, are completely cooled in the coolers, 1 and 2, thereby condensing the tarry vapors and also the aqueous vapor containing most of the ammoniacal and other fixed salts, as well as some free ammonia; these oily and aqueous condensates are collected and saturated by gravity in tank 3. The gases of carbonization, after having thus been cooled, pass through a gasblower, 4, and a Pélouze tar-extractor, 5, which separates the residual tarry vapor, and without being reheated, are conducted through pipe 6 into a lead-lined saturator, 7.

The condensed ammoniacal liquor from tank 3 is delivered, by means of pump 8, through pipe 9, into ammonia still 10, an alkali, such as lime, being also introduced, and into which still, the blower 11 forces, through pipe 12, and superheater 13, a current of hot air, hot products of combustion, or any other hot neutral gases which do not permanently combine with ammonia. The ammonia thus liberated passes through pipe 13 and superheater 15 into saturator 7.

The saturator 7 is divided into two compartments by means of the diaphragm 16, which dips into the acid solution of ammonium salts contained in the saturator 7. The gases of carbonization enter into one of these compartments through the perforated end of pipe 6, pass up through the acid solution, and leave the saturator, after having thus been freed from resid-

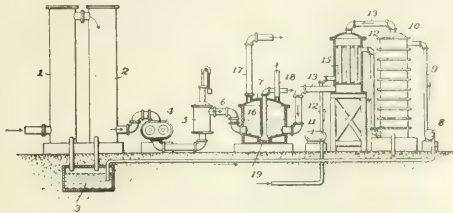


apertures through which intake pipe D, exhaust pipe H, thermometer pipe F, and pressure pipe G communicate with the interior of pot A.

I is a hand-hole closed by a suitable cover, M.



ual ammonia, by means of pipe 17. The vapors from the ammonia still 10, enter the other compartment of the saturator 7 through the perforated end of pipe 13. The contained ammonia is thereby absorbed, while the aqueous vapor and noxious gases which may contain hydrogen sulfid and other gaseous sulfur compounds, hydrocyanic acid, carbonic acid and traces



of hydrochloric acid pass out of the saturator through pipe 18; the effect of superheating of the vapors coming from the ammonia still 10 being to prevent condensation of water in the saturator 7, and thereby a lowering of the concentration of the acid solution which would prevent the ammonium salt from separating in the solid state.

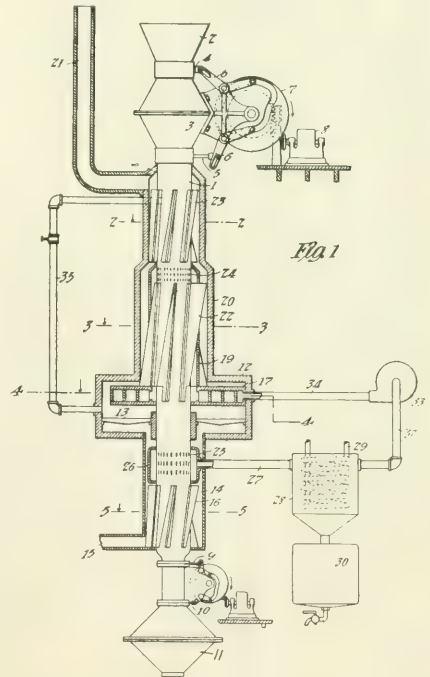
**970,364. Process of Distilling Coal.** JONAS W. AYLSWORTH, of East Orange, and FRANK L. DYER, of Montclair, New Jersey. Patented Sept. 13, 1910.

This invention consists in a process which has been devised for eliminating the smoke-producing elements of soft coals, although other materials may be successfully treated, since the process followed is a special distillation, which is applicable to the treatment of other distillable substances.

The still 1 is a long vertical tube, preferably flaring from top to bottom, so as to facilitate the passage of material through the same. At the top is a hopper, 2, beneath which is a buffer hopper, 3, gate valves, 4 and 5, at the bottom of the hopper 2 and at the bottom of the buffer hopper 3, respectively, being alternately operated so as to permit successive charges of solid material to enter the still, without breaking the seal at the upper end. These gate valves are intermittently operated by any suitable mechanism, as for example, the levers 6, 6, actuated by a cam 7, slowly driven by a motor, 8, as shown. At its bottom the still is provided with intermittently operated gate valves, 9 and 10, actuated by similar mechanism, and opens into a receiving bin, 11, in which the material may cool somewhat before being discharged into the atmosphere.

Surrounding the still is a furnace, 12, having grate bars, 13, and supplied with air through a flue, 14, which envelops the still, and having an inlet, 15, leading to the atmosphere. A series of inclined wings, 16, made preferably of copper, extend through the walls of the still and project into the flue 14 and within the still (see Fig. 5), whereby the material passing through the still will be checked in its descent, and pressure on the still walls, due to the height of the column of material, will be relieved and the material will be more or less agitated. The principal function, however, of these inclined wings, is to act as heat conductors for carrying off the heat from the material into the flue 14, so as to heat the air passing through the flue to the furnace. This acts as a regenerative device, heat being abstracted from the treated coal, or other material, and being imparted to the incoming combustion air. The inclined wings are, therefore, made preferably of copper or aluminum, so as to readily conduct heat. Mounted in the furnace 12 is a drum, 17, having a spiral flue, 18, which opens into a space between the still and a jacket, 19. Outside of the jacket 19 is a second jacket, 20, acting as a stack for carrying off the products of combustion from the furnace 12 and connect-

ing at its upper end with a stack flue, 21. Inclined wings 22, similar to the wings 16, extend into the still and pass through the wall 19, so that heat from the products of combustion passing through the stack will be conducted and imparted to the material undergoing distillation. The inclined wings 22 also serve to check the passage of the material through the still, to partially support the same, and to keep the material in movement, so as to permit the more ready passage of the distillation gases through the material, as will be explained. At the upper end of the still a third series of inclined copper plates, 23, are arranged within the still and extend into the stack 20, so as to convey heat from the products of combustion on the material within the still. The distillation zone of the still is formed between perforations 24 and 25, the former being located within the upper end of the chamber, formed by the partition 19. Surrounding the perforations 25 is a jacket, 26, from which a pipe, 27, leads to a condenser, 28, of any suitable type, that shown being provided with a coil, 29, through which cooling water circulates. The distillate separated by the condenser falls into a tank, 30, from which it may be drawn off by a pipe, 31. Leading from the condenser 28 is a pipe, 32, connected with an inlet to a pump blower or compressor, 33, the discharge from which connects by a pipe, 34, with an inlet to the flue, 18, of the drum 17. With the apparatus shown, provision is made for carrying on the distilling process at atmospheric pressure and to this end a pipe, 35, leads from the upper



part of the still to the furnace 12, so as to carry off any excess gases accumulating in the still. The operation of the still may be carried on below or above atmospheric pressure if desired.

In carrying the process into effect, and assuming the apparatus to be used for the treatment of soft coal, so as to

eliminate the smoke-producing ingredients therefrom, we charge the still with the material through the gate valves 4 and 5, whereby the material will slowly progress through the still, being withdrawn at the lower end through the gate valves, 9 and 10. As the material passes over the inclined wings 23, heat will be imparted to the same, since these wings will be kept hot by the products of combustion from the furnace 12, and, of course, the material will also be heated through the

strata of unlike metals welded together (such as iron or steel, autogenously and completely welded to copper, silver, gold, brass, bronzes, aluminum, etc.).

In the accompanying illustration, in which is shown apparatus for carrying out this process, 1 designates a heating bath termed, ordinarily, the flux bath, containing molten cuprous chlorid, borax, fluor spar, cryolite, or other fusible material which will serve to heat the core to an approximation to the welding heat while preventing oxidation thereof. 2 designates the final heating and filiming bath, containing the super-molten coating metal (copper in the instance assumed) for forming the cohering film on the core. In order to prevent oxidation of the metal of this bath, and also to cover the filmed core with a protecting coating when said core is withdrawn from this bath, the surface of the bath is covered with a layer of molten flux or borax, 3, or other material suitable for the purpose. 4 designates heating means for said baths, the particular means illustrated being a reverberatory furnace, though in lieu thereof any suitable heating means may be employed. 5 designates elevating and traversing means for handling the core, the particular means illustrated being power hoist and traveling crane. 7 designates the core.

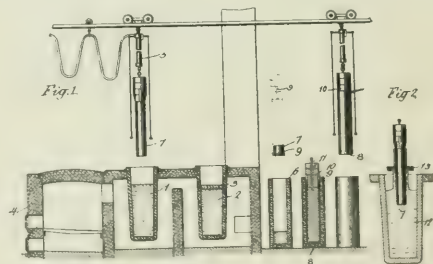
In carrying out the process, the core 7, which has first been cleaned so that it presents an actual metallic surface entirely uncontaminated and chemically clean, is immersed in the heating bath 1, preferably of cuprous chlorid and allowed to remain therein until heated to the proper temperature.

The core, when heated in the flux bath to the proper degree, is withdrawn therefrom and immersed in the filiming bath 2, the flux on the surface of the core rising to the surface of the bath as the core descends, thus exposing an absolutely clean surface to the supermolten coating metal, excluding air from the surface of the core, and avoiding the carrying of the air down into the molten metal. Said molten metal being in the supermolten condition, above described, in which it appears to be chemically active, raises the core to the welding temperature (if said core is not already at that temperature), and what may be an alloy film is formed next the core, the molten metal apparently uniting chemically or by a solvent action with the steel. The core so filmed is then withdrawn from bath 2, dipped in a bath of molten metal, 12, maintained near its point

walls of the still. As the material reaches the distilling zone between the perforations 24 and 25, it will encounter a flow of non-oxidizing heated gases circulated by the pump or compressor 33, through the flue 18, thence between the still and jacket 19, into the perforations 24, the gases leaving the still through the perforations 25, and passing through the condenser 28, by which the condensable ingredients will be removed, thence again to the compressor. These gases will be heated in their passage through the drum 17, as well as in their passage in contact with the wings 22, which wings will be heated by the escaping products of combustion from the furnace. Care should be taken so as to maintain the temperature of the circulating gases between 550° and 800° F., so as to eliminate the desired smoke-producing ingredients, but, of course, the amount of fuel used and the temperature will be regulated according to the material to be treated. As the gases accumulate in the still in excess of those required in the circulating system, they will escape through the pipe 35 and be consumed in the furnace, or they may be used industrially in any other desired way. The treated material leaving the still passes over the inclined wings 16, and imparts heat to the same so as to heat the incoming air to the furnace, as explained.

971,136. Process of Producing Compound Metal Bodies. JOHN FERREOL MONNOT, of New York, N. Y. Assignor to Duplex Metals Company, of New York. Patented Sept. 27, 1910.

This invention relates to a process of producing compound metal bodies, such articles comprising ingots, plates, sheets, rods, tubes, wire and other articles, composed of layers or



of solidification, and then withdrawn from such bath, 12, with the adhering mass of metal from said bath, 12, any excess of metal from said bath being scraped off if desired by passing the ingot through a suitable scraping gage, 13.

Instead of dipping the filmed core into a bath of molten metal maintained at such temperature that upon withdrawal a considerable mass of metal from such bath will adhere thereto, the filmed core may be placed within an ingot mold, 6 (see Fig. 1), such mold having preferably been charged previously with the required quantity of molten coating metal required for forming the predetermined thickness of coating, such molten metal rising up around the core as it ascends into the mold

and completely filling the space between the core and the inner surface of the mold. Union between the molten metal and the film coating takes place very rapidly, and such union is assisted and indeed compelled by the pressure due to contraction of the coating during and after solidification, reinforced usually by pressure due to passing the ingot between the rolls or by hammering or the action of a press. A complete weld and sound coating is thereby formed.

After the formation of the coating as thus described, the ingot is customarily worked between rolls, in a press, or under a hammer to condense the metal of the coating.

## INDUSTRIAL AND TRADE NOTES.

### NEW JAPANESE PAPER MILL.

[From Consul-General Thomas Sammons, Yokohama.]

At Tomakamai, in Hokkaido, Japan, a \$4,000,000 paper-mill plant was completed in August, 1910. This is the most important individual commercial enterprise of this nature in the Far East. Only one foreigner is employed, being an American, who was sent out to assist in installing the paper-making machinery.

The total cost of the machinery of this modern plant is placed at \$1,000,000. Of this all but 3 per cent., it is stated, was purchased in America. An inspection of the plant shows that all the heavy machinery—in fact, practically all of the machinery proper—was manufactured by well-known paper-mill machinery establishments in the United States, mostly by the Bagley Sewall Company, of Watertown, N. Y. A few of the smaller parts, including shafting, were made in Japan, and constitute the 3 per cent. referred to.

The cost of the electrical machinery in this plant, all of which was imported from America, is placed at about \$1,000,000. This does not include the cost of the reservoir and power-house plant, located 14 miles distant, at Lake Shikatsu. This lake is 800 feet above sea-level, and as the paper plant at Tomakamai is only a few feet above the near-by Pacific Ocean, excellent power facilities have been provided. Already a 15,000-horse-power plant has been developed, to which 7,500-horse-power will be added. As the paper plant requires only 8,000-horse-power, it is proposed to sell the surplus (14,500-horse-power) for commercial purposes.

The daily output of the Tomakamai paper-mill plant is upward of 70 tons per twenty-four hours. This is considerable over 50 per cent. of the total consumption of news and book paper in the Empire of Japan. Moreover, it is estimated that the timber supply available for this plant will not be exhausted for half a century or more. Some experts claim that the timber supply in this case will not be used up for over one hundred years. The timber areas include state and railroad lands in addition to privately owned tracts.

Those concerned in this enterprise, being all Japanese, state that the selling price on the tonnage basis of their product will, for the present, be placed at 2.5 to 3 cents per pound. It is evident that this will net a handsome profit, and that the reduced cost of production will enable the Japanese manufacturer to cut prices if necessary to secure a ready market for the output. It is also evident that Japan will export large quantities of paper in the future, the wages paid the ordinary laborer in the Tomakamai plant being approximately \$15 per month.

The Tomakamai plant was planned by a Japanese subject, Mr. Naoki Takata, chief engineer and manager of the manufacturing and construction departments of this plant. He has been engaged in the manufacture of paper in Japan for sixteen years, and for six years has directed all of his time and energies to evolving this new industrial property. He has visited the paper manufacturing centers of the world, and is of the opinion

that the manufacture of paper will become an important industry in Japan.

Mr. Takata states that he has heretofore pointed out to foreign capitalists the inviting possibilities of this industry, but thus far with no practical results, no foreigners becoming interested.

After examining modern American paper-mill plants, Mr. Takata decided that if sufficient water power could be developed in Hokkaido, where coal and timber are plentiful, this industry would prove successful. After locating the necessary water power possibilities at Lake Shikatsu his plans were approved by Japanese capitalists.

Mr. Takata has placed in the Tomakamai plant his own personal inventions for washing the pulp. This plant is also provided with another Japanese invention, the Miyabara naval boiler, of which there are 10, each of 300-horse-power, or a total of 3,000-horse-power boiler capacity.

The electrical machinery, all of American manufacture, includes five 750-horse-power motors; four 450-horse-power motors; forty-three from 100 to 200-horse-power motors.

The floors are all concrete and the buildings are of brick.

### PHOSPHATE DEVELOPMENTS IN OCEANIA.

[From Consul Julius D. Dreher, Tahiti, Society Islands.]

As previously reported by this consulate, deep-sea moorings were purchased in San Francisco by the French Phosphate Company, of Oceania, to replace those lost in the wrecking of the new Norwegian ship, Ocean Queen, at the island of Makatea, on September 16, 1909.

Heavier moorings being necessary, another Norwegian ship, the "Promise," has succeeded, under the superintendence of the mooring master from Ocean Island, in laying these at a distance of 150 fathoms from the shore and in water 225 fathoms deep, which is said to be the greatest depth at which such moorings have ever been anchored. To prevent the slipping of the anchor on the inclined bottom of the ocean, the immense buoy, 11 feet in diameter and 16 feet high, is securely held in position by two cables which are firmly fastened to the shore. As there is no harbor at Makatea, large ships will be moored to the big buoy, while other vessels will be accommodated by the four smaller boys which support the two cables.

A difficult problem at Makatea is an adequate supply of labor. As native labor is scarce, it was supposed from the beginning that when the operations at Makatea reached a certain stage it would become necessary to import Chinese or Japanese laborers, as has been done at Ocean Island. As a result of the importation of Chinese to cultivate sea-island cotton in Tahiti during the civil war in America, there are now in this colony about 800 of these industrious people. They control a large share of the retail trade, of curing and shipping vanilla, or raising vegetables for market, and of baking bread for the natives throughout the island.

Recently a special tax has been imposed on Chinese and also upon the value of buildings occupied by them for business purposes, but still they continue to come to this island, 177 having arrived since the first of the year, and 67 by way of San Francisco and 27 by way of Sydney within the last six weeks. The Phosphate Company entered into negotiations to obtain labor from Japan, but it has been found impossible to import Japanese laborers under a contract binding them to deportation in a specified number of years. In the last few months 27 Japanese mechanics have been imported by way of San Francisco, and they are giving great satisfaction. It seems to be necessary for the company to import ordinary laborers from Japan.

The total working force on Makatea, including superintendents, clerks and craftsmen, numbers a little more than 300, for all of whom this company has to furnish board and lodging.

The island of Makatea, which is situated in the extreme



northwestern part of the extensive Tuamotu Archipelago, has an area of about 10 square miles, one-fifth of which is covered with deposits of phosphate estimated at 10,000,000 tons, of an average grade of 82 per cent. So far as is known here, nothing further has been done to develop the phosphate discovered on Henderson (or Elizabeth) Island, a British possession lying 300 miles east of the limits of this consular district, as was reported by this consulate in *Daily Consular and Trade Reports* of March 12, 1909. As that island is of an elevated coralliferous limestone formation like Makatea, Ocean, Pleasant, and Angaur, it is highly probable that further investigations will show conclusively that the deposits on Henderson are large and valuable.

The world's annual production of phosphate rock is about 5,000,000 tons, the United States being the largest producer, with an annual output of more than 2,000,000 tons. Tunis, which ranks second, produced phosphate of a rather low grade to the amount of \$6,117,000 in 1908. In 1909 the great Gafsa Company, which owns its own railroad, mined 907,000 metric tons (metric ton = 2,204.6 pounds). It pays a large dividend on its capital of \$7,750,000, as is shown by the fact that the stock of this Tunisian company is selling in Paris at a premium of more than 600 per cent. The Pacific Phosphate Company, of London, which owns deposits of 50,000,000 tons of high-grade phosphate on Ocean and Pleasant islands, is mining some 250,000 long tons a year at a profit of more than 50 per cent. on its capital stock of \$1,216,600. A German company has recently begun to mine phosphate to a considerable extent on the island of Angaur, which lies in the western part of the Carolines at no great distance from the Philippines.

As the Pacific Phosphate Company, which has not yet mined 4 per cent. of its immense deposits, could largely increase its annual output; as the production at Angaur will become large in a few years; as Makatea ought to send to the markets of the world several hundred thousand tons of phosphate in the near future; and as the exploitation of deposits in Tunis and Algeria, as well as in other countries, is being carried on actively and extensively, the question arises as to whether the production of phosphate may not soon exceed the world's demand.

But it may be said with some degree of confidence that the increasing attention given to scientific agriculture in most countries of the civilized world will result in a demand for larger and larger quantities of the commercial fertilizers manufactured from phosphate rock, and hence it may be regarded as fortunate that the world's supply of phosphate is being increased from year to year. Even if competition should cause a considerable reduction in the price of phosphate, there would still remain a fair margin of profits for the great operating companies.

#### A NEW ALLOY.

[From Consul Charles N. Daniels, Sheffield, England.]

The Sheffield newspapers announce the discovery and patenting by a Sheffield concern of a new metal or alloy to which the name of "Duralium" has been given, and that it will be manufactured in Birmingham and put upon the market in October.

They believe this alloy to be superior to anything heretofore discovered. Being slightly heavier than aluminum and as strong as steel, it can be rolled, drawn, stamped, extended, or forged at suitable temperatures; it is less corrosive than other high aluminum alloys under the usual corrosion tests, and it is only one-third the weight of brass.

It is expected that the new metal will find a steadily increasing demand for aviation uses, while it is likely to prove an important factor in the construction of motor cars, owing to the difficulty of securing aluminum castings sufficiently reliable not to break under the strain of sudden jars and shocks caused by quick stoppages, changes of speed, and jolts upon bad roads.

#### HIGH-VOLTAGE POWER FROM NIAGARA.

[From Consul Harry A. Conant, Windsor, Canada.]

The feasibility of the Ontario hydro-electric commissioner's plan of transmitting electric current from Niagara Falls at a high voltage, on which Windsor's hope of securing current from the government line depended, has been thoroughly demonstrated by severe tests which have been made by the commission on the line between Niagara Falls and Dundas.

Power at a voltage of 165,000 was turned on to the wires, and it is declared that not a spark was noticeable, although the test was 55,000 volts higher than the voltage which will regularly be used.

It is said that the first time the experiment of transmitting electricity at 165,000 volts has been successfully carried out.

The success of the test indicates that the hydro-electric commission has overcome the last of the difficulties in the way of carrying out its power project, and it is a settled fact that municipalities will get power at a lower rate than was at first promised.

#### RESINITE AND BAKELITE INVENTIONS.

The inventor of bakelite, Dr. L. H. Baekeland, of New York, with a view to preventing infringements, requests the Bureau of Manufacturers to invite attention to the fact that bakelite, which, as has been stated in the *Daily Consular and Trade Reports*, has some analogy with the German product called resinite, is protected in the United States by patents Nos. 939,966, 941,605, 942,699, 942,700, 942,808, 942,809, 942,852, 949,671, 954,666, 957,137, to which patents those interested are referred.

#### GUAYULE RUBBER SUPPLY IN MEXICO.

[From Consul Luther T. Ellsworth, of Ciudad Porfirio Diaz.]

Robert W. Dowe, United States collector of customs for the ports on the Mexican border between San Antonio and El Paso, Tex., verifies my statement in *Daily Consular and Trade Reports*, of August 13th, regarding guayule rubber shrub supply in this consular district by saying:

"Most of it is being used by the American manufacturers of automobile tires. A number of big guayule factories in Coahuila and Chihuahua are working night and day.

"It has been estimated that the value of the guayule shrub now standing on the lands of Coahuila is \$65,000,000. There is as much more in Chihuahua and other mountainous Mexican states. The Mexican owners of guayule land are seeing that the shrub is gathered in such a way that the supply will not be exhausted. Plants are being left in sufficient quantities to reseed and replace those which are cut down and taken to market. The demand for the shrub is so great that thousands of men are employed in gathering it.

"The demand for rubber was never so active and the supply is by no means equal to the demand. The Mexican factories have more orders than they can fill, even by operating day and night, and others are being built. The land on which the guayule grew a few years ago was practically valueless. It is now in big demand. With proper conservation it is believed Mexico has an inexhaustible supply."

#### DRIED BANANAS IN EUROPE.

[From Consul-General Robert P. Skinner, Hamburg, Germany.]

Dried bananas and what are known here as dried banana chips have been offered for sale in Germany with increasing commercial success for over two years.

It is impossible to obtain reliable statistics as the import figures are included with those relating to fresh bananas, both the dried and the fresh fruit being free of duty. Importers consulted state that they have been able to sell without diffi-

culty all the bananas shipped to them, and that the difficulty has been rather to obtain the goods than to find a market.

The consumers of dried bananas and banana chips were originally vegetarians who discovered attractive ways of serving them, but there is now a considerable demand for the dried fruit in all classes of society and one susceptible of being extended materially.

Thus far the best dried bananas have been received from Jamaica, which also seems to be the chief country of exportation. The whole fruit is shipped in wooden cases weighing 25 kilos, or 56 English pounds, and chips are received in sacks. Importers are paying 25 marks (\$5.95) per 100 English pounds for goods delivered in Hamburg, at which price a fairly remunerative business can be carried on. Any substantial increase in the wholesale price would react unfavorably upon the consuming market. (A list of Hamburg firms who might be addressed in regard to dried fruit may be secured from the Bureau of Manufacturers.)

#### ENGLISH SLAG PAVING BLOCKS.

[From Vice-Consul H. Nixon, Newcastle-on-Tyne.]

Scoria bricks, or slag paving blocks, have been manufactured in the Middlesbrough district for many years, and considerable quantities have been shipped to the United States since 1894. (A shipload was recently received at Washington, D. C.)

The bricks are manufactured from molten slag from the blast furnaces. The slag is drawn from the furnace into iron caldrons lined with fire-brick. These are mounted on bogies, for transmission to the brick plant. The slag is poured from these caldrons into iron molds. These molds are made with a hinged bottom and are mounted on the circumference of a circular iron framework. This revolves and allows the molds to be filled separately. As the bricks solidify they are removed and placed in a beehive oven, where the residual heat anneals the whole of the brick.

#### AIR-NITRATES IN THE UNITED STATES.

Mr. W. S. Lee, Jr., Vice-President of the Southern Power Company, of Charlotte, N. C., has gone to Europe, where he will spend several weeks in the interests of the plants his company proposes to establish for the manufacture of air nitrate fertilizers. The *Charlotte Chronicle* states that the contract for the first plant, which will be of 4,000 horse-power, has already been let, and some of the machinery for it is being manufactured abroad at this time. The Southern Power Company has acquired the right to use the "Geneva process" of abstracting nitrogen from the air and also rights to use a newer process, and it is in connection with the latter that Mr. Lee goes abroad.

The first plant to be built by the Charlotte Company will be used to a great extent for experimental purposes, and the second, which will require 24,000 horse-power to operate, will be used for the manufacture of nitrate fertilizers on a large scale.

### OFFICIAL REGULATIONS AND RULINGS.

#### FOOD INSPECTION DECISION NO. 126.

##### *Salts of Tin in Food.*

The attention of the board has been directed to canned goods which contain salts of tin derived from the solvent action of the contents of the package upon the tin coating. Pending further investigations on the question all canned goods which are prepared prior to January 1, 1911, will be permitted to enter and pass into interstate commerce without detention or restriction in so far as their contents of tin salt is concerned. All foods which are canned subsequently to January 1, 1911, will be permitted importation and interstate commerce if they do

not contain more than 300 milligrams of tin per kilogram, or salts of tin equivalent thereto. When the amount of tin, or an equivalent amount of salts of tin, is greater than 300 milligrams per kilogram, entry of such canned goods packed subsequently to January 1, 1911, will be refused, and if found in interstate commerce proper action will be taken.

It is the opinion of the board that the trade will experience little hardship in adjusting itself to this condition, as the results of examinations made by the Bureau of Chemistry of various types of canned goods indicate that in a very large majority of cases inconsiderable quantities of tin are found, well within the limit herein set.

H. W. WILEY,

F. L. DUNLAP,

GEO. P. McCABE,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,

*Secretary of Agriculture,*

WASHINGTON, D. C., September 22, 1910.

#### NOTICE OF JUDGMENT NO. 539, FOOD AND DRUGS ACT

##### *Adulteration and Misbranding of Turpentine.*

On or about June 11, 1909, the Gulf Manufacturing Company, Limited, a corporation, New Orleans, La., shipped from the State of Louisiana to the State of Texas a consignment of alleged spirits of turpentine, the packages containing which each bore the following label: "Crescent brand spirits of turpentine. Guaranteed by Gulf Manufacturing Company, Ltd., under the Food and Drugs Act of June 30, 1906 Gulf Manufacturing Company, Ltd., New Orleans, La."

Samples from this shipment were procured and analyzed by the Bureau of Chemistry, United States Department of Agriculture, and as it appeared from the findings of the analyst and report thereon that the product was adulterated and misbranded within the meaning of the Food and Drugs Act of June 30, 1906, the Secretary of Agriculture afforded the Gulf Manufacturing Company, Limited, and the party from whom the samples were procured, opportunities for hearings. As it appeared after hearings held that the said shipment was made in violation of the act, the Secretary of Agriculture reported the facts to the Attorney-General, with a statement of the evidence upon which to base a prosecution.

In due course a criminal information was filed in the Circuit Court of the United States for the Eastern District of Louisiana, charging the above shipment, and alleging that the product so shipped was adulterated, in that mineral oil had been added to the so-called turpentine, and that the product differed from the standard of strength, quality, and purity of oil of turpentine as determined by the test laid down in the United States Pharmacopoeia or National Formulary official on the date of said shipment, the words "Spirits of Turpentine" occurring in the label above set forth being synonymous with and used indiscriminately in this country to designate the same drug as the name oil of turpentine just mentioned; and in that the strength and purity of said product fell below the professed standard and quality indicated by the label aforesaid; and further alleging that the product was misbranded, in that the label above set forth was false and misleading, and such as to deceive the purchaser into believing that the contents of said packages were pure spirits of turpentine, whereas in truth and in fact said contents were not pure spirits of turpentine but a mixture of spirits of turpentine with mineral oil; and in that said label was meant and intended and calculated to convey, and did convey, the impression that the said drug was pure spirits of turpentine, which was false, since the said drug was a mixture of spirits of turpentine and mineral oil; and in that the product was an imitation and offered for sale under the distinct-

ive name of another article, to wit, spirits of turpentine, which it was then and there represented to be by the label, though in truth and in fact it was not spirits of turpentine for the reason that mineral oil had been mixed therewith.

On June 29, 1910, the defendant entered a plea of guilty to the above information, and the court imposed a fine of \$10 and costs.

This notice is given pursuant to Section 4 of the Food and Drugs Act of June 30, 1906.

W. M. HAYS,

*Acting Secretary of Agriculture.*

WASHINGTON, D. C., July 29, 1910.

#### NOTICE OF JUDGMENT NO. 550, FOOD AND DRUGS ACT.

##### *Adulteration and Misbranding of Spirits of Camphor*

On or about February 9, 1909, the Dow & Snell Company, Incorporated, Toledo, Ohio, shipped from the State of Ohio to the State of Michigan a consignment of drug product labeled "Triumph Brand, Pure Spirits of Camphor, manufactured by the Dow & Snell Company, Toledo." A sample from this shipment was procured and analyzed by the Bureau of Chemistry, United States Department of Agriculture, and as it appeared from the findings of the analyst and report thereon that the product was adulterated and misbranded within the meaning of the Food and Drugs Act of June 30, 1906, the Secretary of Agriculture afforded the Dow & Snell Company, Incorporated, and the dealer from whom the sample was purchased, opportunities for hearings. As it appeared after hearings held that the said shipment was made in violation of the act, the Secretary of Agriculture reported the facts to the Attorney-General, with a statement of the evidence on which to base a prosecution.

In due course a criminal information was filed against the said Dow & Snell Company, Incorporated, in the District Court of the United States for the Northern District of Ohio, charging the above shipment and alleging that the product was adulterated in that it was sold under a name "Spirits of Camphor," recognized in the United States Pharmacopoeia, but that the article did not comply with the standard prescribed by that authority and did not have the standard of strength, quality, or purity stated upon the package in which it was contained, and further that the product was misbranded in that the package containing the same was so labeled as to cause the purchaser to believe that the article was spirits of camphor when as a matter of fact it was not spirits of camphor as recognized by the United States Pharmacopoeia, and also that the label in no manner declared the presence of alcohol in the product, when as a matter of fact a quantity of alcohol was found therein.

On June 22, 1910, the defendant entered a plea of *nolo contendere* and the court imposed a fine of \$25 and costs.

This notice is given pursuant to Section 4 of the Food and Drugs Act of June 30, 1906.

W. M. HAYS,

*Acting Secretary of Agriculture.*

WASHINGTON, D. C., August 5, 1910.

#### NOTICE OF JUDGMENT NO. 572, FOOD AND DRUGS ACT.

##### *Adulteration and Misbranding of Gum Tragacanth.*

On or about September 3, 1909, The National Aniline and Chemical Company, a corporation of the Borough of Brooklyn, New York City, shipped from the State of New York to the State of New Jersey a quantity of a drug product labeled "Powdered Gum Tragacanth."

Samples from this shipment were procured and analyzed by the Bureau of Chemistry, United States Department of Agriculture, and as the findings of the analyst and report thereon indicated that the product was adulterated and misbranded within the meaning of the Food and Drugs Act of June 30, 1906, the Secretary of Agriculture afforded said National Aniline and

Chemical Company and the dealer from whom the samples were procured opportunities for hearings. As it appeared after hearings held that said shipment was made in violation of the act, the Secretary of Agriculture reported the facts to the Attorney-General, with a statement of the evidence upon which to base a prosecution.

In due course a criminal information was filed in the Circuit Court of the United States for the Eastern District of New York against the said National Aniline and Chemical Company, charging the above shipment and alleging the product so shipped was adulterated, in that it differed from the standard of strength, quality, and purity of gum tragacanth as determined by the test laid down in the United States Pharmacopoeia or National Formulary official at the time of investigation, and further alleging that said product was misbranded, in that it was sold and shipped under and by the name of "Powdered Gum Tragacanth" when in truth and in fact it was not "Powdered Gum Tragacanth" but a different article, to wit, "Powdered Indian Gum."

On June 1, 1910, the defendant entered a plea of guilty and the court imposed a fine of \$25.

This notice is given pursuant to Section 4 of the Food and Drugs Act of June 30, 1906.

W. M. HAYS,

*Acting Secretary of Agriculture.*

WASHINGTON, D. C., August 20, 1910.

#### NOTICE OF JUDGMENT NO. 583, FOOD AND DRUGS ACT.

##### *Misbranding of Asafetida.*

On or about January 21, 1909, Albert Bruen, William P. Ritchey, and Charles C. Bruen, doing business under the first name of Bruen, Ritchey & Co., New York City, shipped from the State of New York to the State of New Jersey a quantity of a drug product contained in a package labeled: Gum Asafetida (*Foetida ferula*) 1 pound Bruen, Ritchey & Co., New York. Guaranteed under the Food and Drugs Act, June 30, 1906. Serial No. 1063.

Samples from this shipment were procured and analyzed by the Bureau of Chemistry, United States Department of Agriculture, and as the findings of the analyst and report made indicated that the product was misbranded within the meaning of the Food and Drugs Act of June 30, 1906, the said Bruen, Ritchey & Co., and the party from whom the samples were procured were afforded opportunities for hearings. As it appeared after hearings held that the shipment was made in violation of the act, the Secretary of Agriculture reported the facts to the Attorney-General, with a statement of the evidence upon which to base a prosecution.

In due course a criminal information was filed in the Circuit Court of the United States for the Southern District of New York against the said Bruen, Ritchey & Co., charging the above shipment and alleging that the product was misbranded, in that the label above set forth was false and misleading because it represented the product to be "asafetida" when, as a matter of fact, it contained much foreign material.

On April 5, 1910, the defendants entered a plea of guilty to the above information and the Court imposed a fine of \$50.

This notice is given pursuant to Section 4 of the Food and Drugs Act of June 30, 1906.

W. M. HAYS,

*Acting Secretary of Agriculture.*

WASHINGTON, D. C., August 27, 1910.

#### CORRECTION.

An error was made in reporting the carbonates in the Columbia River water which appeared in the June number of THIS JOURNAL. The CO<sub>2</sub> should read 11.0 parts per million instead of 1.1 as reported.

C. E. BRADLEY.



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## EDITORIALS.

### THE QUALITY OF PLATINUM.

IN recent years there have been many complaints about the quality of the platinum ware used in the chemical laboratory. It has been said that platinum ware of the present day is not as good as that manufactured some years ago. Very recently several large lots of platinum dishes and crucibles have been returned to the makers on account of alleged inferiority, by different Bureaus of the United States Government. Platinum is of fundamental importance in analytical chemical work. In spite of the substitution of silica ware and apparatus for platinum for certain purposes, the metal remains indispensable for many chemical operations. But it should be pure. If pure, durable platinum ware could be manufactured in former years, there is no reason why as good or better ware cannot be made to-day. With improved gas and electric furnaces, and a variety of means for obtaining and controlling high temperatures, the working of platinum should be easier to-day than ever before; methods of chemical analysis have also been improved even if methods of chemical purification have not to any great extent. The chief complaints which have been made would seem to indicate gross carelessness or lack of skill in manufacture, for it is said, for example, that certain plat-

inum ware developed a white layer on exposure to high temperatures; other pieces developed cracks when heated; other pieces gave up several milligrams of iron when digested with hydrochloric acid. All platinum ware is expected by the chemist to withstand certain simple tests. It should not change color, lose weight, develop cracks, or show a whitish coating after being heated to a high temperature for several hours in the blast flame or furnace. It should not be brittle and should be durable. It should show only an insignificant loss in weight when digested with hydrochloric acid. It is to be hoped that the reported inferiority of some of the modern platinum ware will speedily be corrected. This would be to the best interest of the manufacturers. Poor platinum ware inevitably leads the chemist to look for substitutes—in some cases successfully. It is said that the Bureau of Standards at Washington has contemplated for some time an investigation of the whole subject of the quality of platinum apparatus and ware. It would be well if the manufacturers would lend their coöperation in this work. That the results of such an investigation would be of the greatest interest to the chemical profession does not require emphasis.

### THE PRICE OF POTASSIUM SALTS.

ACCORDING to the calculations of Dr. F. W. Clarke, potassium ranks seventh in point of abundance among the elements composing the chemically-known earth. The elements and their relative abundance down to and including magnesium are: Oxygen, 49.78 per cent.; silicon, 26.08 per cent.; aluminum, 7.34 per cent.; iron, 4.11 per cent.; calcium, 3.19 per cent.; sodium, 2.33 per cent.; potassium, 2.28 per cent.; magnesium, 2.24 per cent. In commerce the greatest outlet for potassium is in the fertilizer trade. Of the ten or twelve elements which enter into the composition of the higher plants and which are necessary for their growth, potassium occupies an important place. Without potassium in the form of soluble salts the higher plants cannot grow and develop to maturity. And, unfortunately, it is one of the elements in which soils are likely to be deficient in available condition. Therefore it is necessary to apply potash salts to the soils as fertilizers and the use of potash salts for this purpose is increasing at an enormous rate. Potassium is found in insoluble condition in the feldspathic rocks and others, and in

soluble compounds in the ocean. In insoluble condition in the igneous rocks it is found to the extent of about 2.45 per cent., in the ocean about 0.04 per cent. Thus the world's great source of potassium is locked up in insoluble condition. It is true that weathering converts insoluble potash into soluble salts, but it is also true that these soluble salts have a great tendency to leach away. And unless the process is continuous in the soil it will be lacking in potash. Practically, the whole world is dependent on one source of supply of potassium salts, namely, the so-called Stassfurt beds in Germany. These beds were formed by the crystallization of the salts in the mother liquors of ocean water from which common salt had separated. In most localities where salt beds and gypsum are found—for example, in the states of Michigan and New York—no potash deposits are found. Evidently the mother liquors in these cases drained away without crystallizing. The German deposits are therefore unique. In them Germany has a great national asset. The United States, a great agricultural nation, is dependent on the German supply of potash for fertilizer. We consume annually more than one-half the total amount exported from Germany, at a cost of about \$8,000,000 per year. Before the first of the present year many large American fertilizer manufacturers had signed favorable contracts with certain potash mines which were "independent" in the sense that they did not belong to the "Syndicate." When it became evident that potash salts would be sold in America largely by producers who were not in the Syndicate, a law was passed by the German Reichstag which in effect, by indirection, made these contracts ineffective and non-operative. American manufacturers have been forced to buy potash salts at Syndicate prices in spite of their contracts with the independent mines.

The price paid per ton of muriate of potash is now \$34.00 instead of \$20.40, the price fixed by the contracts. The price of sulphate of potash has risen from \$25.00 to \$43.50 per ton. The very ingenious law by which these changes were brought about in international trade, under the plea that it was a purely domestic affair, is worthy of more than casual perusal. It has aroused the greatest interest at home and abroad and has led to many diplomatic representations. The German government stands by the Syndicate and thus far all the proposals of the American representatives have proven fruitless. What the final consequences will be it is impossible to foretell. A tariff war has been predicted. It is said that the United States government is considering the advisability of imposing maximum tariff rates—25 per cent. above the minimum now enjoyed—on imports from Germany. German newspapers say the Americans are only bluffing.

It has been said that in the United States a man runs the risk of fine or imprisonment if he belongs to a trust; on the other hand, abroad, a man runs the same risk if he does not belong to the trust. Recent developments in the German potash situation lend argument to these assertions.

With the advent of high-level potash prices, the search for new and cheaper sources of supply will go forward with renewed energy, and probably with success at no far distant day. The supply of insoluble potash in feldspar and other silicate minerals will offer tempting possibilities to the industrial chemist, and as the successful solution of the problem rests largely on the ability of the product to stand freight charges it is not improbable that at the present prices an industrial process will be devised which will be cheap enough to interest capital.

#### THE APPLICATION OF SCIENCE TO INDUSTRY.

IN one of the ponderous volumes containing the works of the Honourable Robert Boyle is to be found an essay entitled "That the Goods of Mankind may be, much Increased by the Naturalist's Insight into Trades." To the modern ear these words have a wonderfully familiar ring. In our own times there has been laid increasing emphasis on the necessity for closer interrelationship between science and industry for the betterment of both, so that the doctrine, if not the application of it, has become a commonplace. Some of us have supposed that our views on this subject were quite modern, not to say one of the signs of our times. Nevertheless, much of this essay of Robert Boyle's, written in the sixteen hundreds, if it were divested of its oftentimes painful precision of expression and undue elaboration and transposed into a modern English style, would do credit to a present-day document. In thought it belongs to the present, not to the past. At the beginning of his discourse Boyle says: "To make out what is proposed in the title of this discourse, I shall endeavor to show two things. The one, that an insight into trades may improve the naturalist's knowledge. And the other, that the naturalist, as well by the skill thus obtained, as by the other parts of his knowledge, may be enabled to improve trades." This is a most concise and comprehensive statement of the whole modern situation. Boyle continues: " \* \* it seems to me none of the least prejudices. \* \* \* that learned and ingenious men have been kept such strangers to the shops and practices of tradesmen. For there are diverse considerations that persuade me, that an inspection into these may not a little conduce, both to the increase of the naturalist's knowledge and to the melioration of those mechanical arts." Throughout the essay Boyle shows a keen appreciation of the materials of education

which exist in the workshop and factory, and how they may be utilized to advantage by the scientist. That he himself frequently utilized knowledge acquired in the shops is shown further on.

"And I consider, in the first place, that the phenomena afforded by trades, are (most of them) a part of the history of nature, and therefore may both challenge the naturalist's curiosity and add to his knowledge. Nor will it suffice to justify learned men in the neglect and contempt of this part of natural history, that the men, from whom it must be learned, are illiterate mechanics, and the things that are exhibited are works of art, and not of nature." "For besides, that many of those productions which are called artificial, do differ from those that are confessedly natural not in essence, but in efficients; there are very many things made by tradesmen, wherein nature appears manifestly to do the main parts of the work: as in malting, brewing, baking, making of raisins, currants, and other dried fruits; as also hydromel, vinegar, lime, etc., and the tradesmen does but bring visible bodies together after a gross manner, and then leaves them to act one upon another, according to their respective natures; as in making of green or coarse glass, the artificer puts together the sand and ashes, and the colligation and union is performed by the action of the fire upon each body."

There must have been a great change of sentiment among chemists from Boyle's time to ours. Then it seems it was necessary to persuade them of the advantages of entering into factories and workshops to observe the operations; on the contrary, to-day it takes the best efforts of many manufacturers to keep them out.

"I have several times observed trades deal with things unknown to classical writers, and unused, save in their shops. And these are not only factitious but divers of them natural; as manganese (by some called magnesca), zafora (if at least it be what many repute it), emery, tripoli, etc., and of both sorts there are some that are exceeding useful; as of those formerly mentioned, the two first are to glassmen and potters; and the two latter to a number of other tradesmen; and as among artificial concretes, soaders are of necessary use to goldsmiths, locksmiths, coppersmiths, braisiers, pewterers, tinmen, glasiars, etc., amels to goldsmiths, glassmen, etc., lakes of several softs to painters, heralds, etc., and putty to amel founders, potters, stonecutters, goldsmiths, glass grinders, and divers other professions."

"And I freely confess to you, *Pyrophilus*, that I learned more of the kinds, distinctions, properties, and consequently of the nature of stones, by conversing with two or three masons, and stone-cutters, than ever I did from Pliny, or Aristotle and his commentators."

That the science of chemistry owes a great debt to

the arts and crafts, and particularly to chemical manufacturers, cannot be gainsaid. The phase of Boyle shown by these quotations, wherein he, the aristocrat in this search for truth, is seen conversing with workmen in the various trades, inquiring into factory processes and in general availing himself of materials of education which in his day were too evidently considered unprofitable and undesirable is most interesting. He speaks of brewers, tanners, glassworkers, goldsmiths, locksmiths, pewterers, tinsmiths and many others as though he were on easy terms with them and their professions. He also learns matters of historical interest for he says: "By frequenting the workhouses and shops of craftsmen, a naturalist may often learn other things, besides the truth and falsity of what they relate, concerning the history of the arts they make profession of." And a little further along he shows his appreciation of the historical treatment by remarking: "For I look upon a good history of trades, as one of the best means to give experimental learning both growth and fertility, and like to prove to natural philosophy what a rich compost is to trees, which it mightily helps, both to grow fair and strong, and to bear much fruit." He tells how he learned the art of making fine powders by elutriation and sedimentation from the plaster of Paris molders. He even thought "to bind several ingenious lads apprentices to several trades, that I might the better, by their means, both have such observations made as I should direct, and receive the better historical accounts of their professions, when they should be masters of them." But not alone did he receive instruction from the trades. He suggests ways in which the scientist may contribute to the development of manufacture, and he shows how he himself in several instances was able to improve the methods of his day in certain lines. As to the improvement of manufacture by the scientist, he says:

"This he may do by several ways, and especially by these three. The first, by increasing the number of trades by the addition of new ones. The second, by uniting the observations and practices of differing trades into one body of collections. And the third, by suggesting improvements in some kind or other of the particular trades."

"The artificer may be too much confined to certain materials, some of which may be scarce, or dear, or ill conditioned, in comparison of others that the naturalist might propose. As I remember, that being in a place, where we could not produce good vitriol to make aqua fortis with, after the manner of our English refiners, by a substitution of burnt alum for vitriol, but in a far less proportion, we made solvents for silver, as good as theirs, if not much better."

"For there are many things, which he who is acquainted with variety of bodies, and the accounts on which they work on one another, will either quickly



discern to be performable by other materials, than those that tradesmen confine themselves to, or probably guessed to be performable by other agents more in the tradesmens power; and by making trials of his conjectures, it is like he will within a few trials discover what he seeks."

He also sets many practical problems for the scientist to investigate and solve: " \* \* \* \* " the cracking of glass of its own accord, and particularly that which is complained of by divers who deal in telescopes, that the object-glasses, which are wont to be made, as I was saying, of fine Venice glass, will sometimes, especially in water, flaw of themselves, and so grow useless, to prevent which, some, that are very curious, carry them in their pockets."

" \* \* \* the fading of the bow-dye of water colors in liming, and the rust of shining arms, and other polished steels. Divers of these inconveniences also the naturalist may obviate or remedy; as some of the virtuosi above-mentioned, by teaching the glass-grinders to make the object-glasses of their telescopes of green glass, have taught them a way to make them durable in spite of the vicissitudes of weather."

These are only a few of the problems which he outlines. Many of them would appear foolish or impossible of solution to us. In the first burst of this enthusiasm they did not to Boyle. His clear insight and his great appreciation of the necessity for closer coöperation between science and industry mark him as one who lived before his time. In no other of his essays does his genius show more conspicuously.

## ORIGINAL PAPERS.

### THE BORAX INDUSTRY.

By F. M. DUPONT.

Received October 26, 1910.

It is now about half a century since borax has been commercially manufactured. Since that time the industry has undergone some radical changes. Before going into the details of the process of manufacture, I will mention the different sources of supply. The element boron is widely distributed through the earth crust, even sea water being known to contain minute amounts of borax.

Boric acid is found free in nature in many volcanic districts, as in Tuscany, where the vapors issuing from the saffioni charged with the acid are passed through vats of water until the water becomes sufficiently concentrated, or, are deposited as a crystalline crust around the margins, as in the neighborhood of Sasso. When these little lagoons are sufficiently concentrated with boric acid they are run into crystallizing vats and the product put on the market as sassoline or Tuscany acid:

#### TUSCANY ACID.

	Per cent.
$B_2O_3 + 3H_2O$ .....	83.46
Water.....	1.44
Am. sulph.....	5.30
Mg. sulph.....	7.50
Fe and Al.....	0.30
Sand and organic matter.....	2.00
	100.00

In the United States, it was first found in the water of Clear Lake, in Northern California, which waters, when evaporated, gave borax. Then borax was found in the surface crust of desert marshes in California and Nevada, and later on borax was leached out of the clay formations of the marsh deposits. Lately great deposits of a fairly pure calcium borate have been found in various parts of California, embedded in old tertiary sediments.

There are three varieties of calcium borate which correspond to the varieties of calcium carbonate: calc spar, marble and chalk, viz., colemanite, pandermite and priccite, each found in different parts of the world in large quantities and of a well defined and constant composition.

Further, there is the boronatrocalcite, ulexite, tiza or cotton balls, a sodium calcium borate and the stassfurtite or boracite, a magnesium borate. There are a good many more varieties of natural borates and borosilicates which are of more interest to the mineralogists than to the manufacturer or which belongs to the class of gems and precious stones. The ore most extensively used in the United States is the colemanite.

There are two localities which are now the principal source of supply, the mines in Death Valley and the mines at Lang, near Los Angeles.



Colemanite mine at Lang, California.

The geological formation of the surroundings consist of black lava, sandstone, limestone and clays of different colors. Mining is carried on by means of shafts.

Colemanite is of a crystalline nature and resembles

closely, in its appearance, the calc spar or Iceland spar, for which it has been very often mistaken. Frequently colemanite is also called borspar. The color of the crystals is colorless to white, yellow-white, and gray. The hardness is 3.5 to 4.5. It pulverizes easily but the crystals have very sharp edges and cause a good deal of wear and tear in the pulverizing plant. In the ore, as it is mined, some parts of the colemanite



Bins, colemanite mine at Lang, California

are of a different character and of an exceptional hardness. Chemically speaking, colemanite is a hydrated sesquiborate of lime, differing only in composition as regards water of crystallization. The formula is  $(\text{CaO})_2(\text{B}_2\text{O}_3)_3 \cdot 5\text{H}_2\text{O}$ . In the blow-pipe it exfoliates and decrepitates violently and then sinters and finally fuses completely. The ore, as it is mined, runs from 33 per cent. to 35 per cent.  $\text{B}_2\text{O}_3$ .

The analysis shows, besides boric acid, other impurities differing according to the locality from which the sample came. Below is the analysis of a sample of colemanite from Lang, California:

	Per cent.
$\text{B}_2\text{O}_3$ .....	36.10
$\text{CaO}$ .....	23.74
$\text{Al}_2\text{O}_3$ .....	1.27
$\text{Fe}_2\text{O}_3$ .....	1.32
$\text{MgO}$ .....	2.36
$\text{CO}_2$ .....	5.14
$\text{SiO}_2$ .....	13.97
Water .....	16.10
	100.00

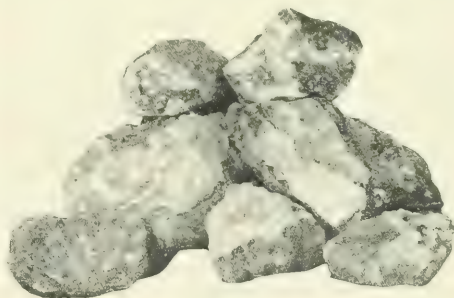
As borax contains 36.67 per cent.  $\text{B}_2\text{O}_3$ , 1 pound of ore will make nearly 1 pound of borax.

Pandermite, or Turkish boracite, is found in Asia Minor. The field is near the Rhyndamus river, whose outlet is in the sea of Marmora, near the Port of Panderna, on the Asiatic shore. This port is regularly frequented by sea-going vessels and gives, therefore, ample facilities for shipping. The field embraces the villages of Sultan, Thair, Yildiz, and Omerly, and covers about twenty square miles and is situated in a basin of tertiary age surrounded by volcanic

rocks, such as granite, trachyte and basalt. Several basaltic hills protrude in different portions of the basin and the presence of hot mineral springs further testifies to the volcanic influences which have been at work and in which, doubtless, originated the boracic acid mineral.

Pandermite occurs in an enormous bed of gypsum, which is covered with several feet of clay. The mineral exists in closely packed nodules of very irregular shapes and sizes, from the size and weight of a walnut up to one ton. The outside crust of this ore is especially hard. It is easily separated from the dark-colored gypsum in which it is embedded. It is sold on the European market on a basis of 44 per cent.  $\text{B}_2\text{O}_3$ . The chemical combination is the same as that of the colemanite, only if heat is applied to it it does not exfoliate but sinters together and fuses to a transparent mass. It resembles closely, in its outward appearance, a fine-grained marble.

Boronatrocaltite is found in Peru and Chile, Province of Otocama, and Ascotan and Maricunga and Copiapo. The crude material, also known as Tiza, occurs in both places, in lagoons and troughs. These, instead of being filled with common salt, as is usually the case, in the desert, contain zones or layers of boronatrocaltite, alternating with layers of salty earth. The raw material from these places varies from 25 per cent. to 45 per cent.  $\text{B}_2\text{O}_3$ . It is shipped



Colemanite

to European ports from Arequipa, Ascotan, Iquique, Bolivia, Tocopilla, Chilcaya and other small places. The chemical formula is  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot \text{Na}_2\text{B}_4\text{O}_7 \cdot 16\text{H}_2\text{O}$ .

#### BORONATROCALCIT FROM ASCOTAN

	Per cent.
$\text{B}_2\text{O}_3$ .....	38.04
$\text{H}_2\text{O}$ .....	19.86
$\text{Na}_2\text{O}$ .....	15.91
$\text{CaO}$ .....	12.34
$\text{MgO}$ .....	0.37
$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ .....	0.24
$\text{SiO}_2$ .....	4.95
$\text{Cl}$ .....	9.64
$\text{SO}_3$ .....	0.84
	100.00

It is a soft, silky, fibrous mineral, brilliant white

when pure, but generally found in nodules of yellowish white color.

Another, but small source of supply, is stassfurtite or boracite, near Stassfurt in Prussia, in the kainite beds. It is a magnesium borate and looks like fine marble, sometimes a soft, slimy mass and sometimes of hardness 7.

I believe this covers all the borates which are at the present time used in the manufacture of borax and boric acid.

The manufacture of borax differs according to the raw materials used, also according to the personal preference of the superintendent and chemist. There is more than one method practicable for the same ore. We will first discuss the methods used if the raw material is colemanite. The ore, as it comes from the mines, is crushed in a stone breaker to the required fineness, which depends on the kind of mill to which it is fed afterwards. The size varies from one-half to one and one-half inches. As the mineral passes through it is taken up by elevators and carried to the mill and from there to a sifting machine. The powder is so fine that it has to go through a bolting-cloth, known as silk No. 8. The fine material is conveyed by means of a screw and elevator into bins capable of holding a certain stock, which seems necessary to have on hand in case an accident occurs to the mill. From here the weighed ore is dumped into the decomposers. Sometimes before, the decomposers have been filled with the remaining mother liquor from the crystals and additional water. After the ore has been dumped in, carbonate and bicarbonate of soda in the right proportion are added and steam turned on. Experience will show how long a certain ore needs boiling. The mother liquor is pumped through filter presses and the clean liquor runs with or without aid of an intermediate settling tank into the crystallizers. The mud in the press chamber is leached out and disposed of. The crystallizers are fitted up with vertical iron rods hanging on bars, about 8 inches from each other. In six to ten days all the borax will be crystallized save a small per cent. which will always remain in the mother liquor. The liquor is siphoned off and the crystals are washed, broken off the rods and sides, dried, and granulated or powdered.

Pandermite cannot be decomposed under the same conditions. The mineral is reduced in about the same way, only a different type of mill is used. The mixture of ore, soda and bicarb and mother liquor is boiled in closed vessels and at a pressure of 60 pounds steam overnight.

In France the pandermite is decomposed with soda ash only in autoclaves. The liquor contains then the biborate and monoborate of soda and to this liquor enough boric acid is added to convert all into

biborate, and then it is handled in the same way as the other ore.

There are a good many more processes, which are of more or less value. In France there is made, besides the regular borax, the octahedral borax, which contains only five molecules of water. In this case the liquors are made more concentrated and then cooled down to 56° C. and siphoned off. This borax is also called jewelers' borax, because it is usually made for jewelers.

The boronatrocalcite is worked up in a similar manner. The operation consists of reducing the



Borax crystals on crystallizing rods.

material in a state of fine division, and for this purpose the mill used is so constructed as to tear the borate ore to pieces instead of grinding it, which, owing to the fibrous nature, is found more profitable. The borate is then mixed with proper proportion of carbonate and bicarbonate of soda. 100 parts of ulexite, 43 per cent.  $B_2O_3$ , require 10 parts of bicarbonate and 12 parts of soda for the conversion into 117 parts of borax.

The uses of borax are various and in nearly every industry borax is used in some department. The



largest use of borax is in enameled sanitary and kitchen ware, and it is the most essential part of the enamel. It is also largely used as a flux in the manufacture of pottery and earthenware glaze. Borax is used in the making of certain varieties of glass and in the manufacture of artificial gems and strass. It is an important substance in the manufacture of optical glass and glass which should not be susceptible to changes of temperature, such as incandescent lamps, lamp chimneys, etc., as such boro-silicate glass has a minimum coefficient of expansion.

It is also used for making vitrifiable pigments for staining glass and in the manufacture of encaustic tiles, which are rendered fusible by its admixture.

Borax is used in the tannery and in the currying shop. It is of great benefit in the soaks, where it dissolves the dirt and the blood and insures a more rapid liming. In the bates for sole and chrome stock, a borax bath has been found very commendable.

It is also used in the first stage of tanning in the liquor. It is used for cutting the oils and fats used in stuffing leather. Borax is also one of the best known agents for whitening and bleaching leather of all kinds; especially russet leather is treated with borax. It is the best known mordant for coloring leather. It really replaces any alkali used in tanning, on account of being more harmless, antiseptic and sweetening.

Borax, for its great cleaning properties, is used in the laundry in washing as well as in the starching. There are several starches on the market containing borax, its admixture helps to give the shirts and collars a very high gloss. Borax is also used as a wood preservative against dry rot.

Another very large use is as a flux for welding and brazing metals on account of its capacity of easily dissolving the metal oxides and leaving a blank surface. The jewelers use it also for the same purpose.

Varnish made by boiling one part of borax with five parts of shellac is used for stiffening hats. With casein borax forms a substitute for gum which is moisture-proof. The paper mills use it for making a kind of parchment which is fat and waterproof. It is also used in the making of certain sizes and coatings for glazed papers and playing cards.

On account of its antiseptic qualities it is used in pharmacy in cosmetics, mouth washes, tooth powders and salves. The dentists use it for cleaning the teeth. It is used as an admixture for powders for killing insects, roaches, etc. It is also used as a preservative for meats and other foodstuffs, and finally in the manufacture of other boron compounds.

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## WATER PROBLEMS.

By WILLIAM M. BOOTH.

Received November 3, 1910.

On the average more than two hundred gallons of water fall annually per square yard on the territory east of the Mississippi river. This is soft and reasonably clean.

To ascertain some of the properties of precipitated water, I have analyzed samples of snow that fell two miles from the center of Syracuse, outside my residence. The first sample was taken one evening in February, 1910. This analysis is as follows:

### NO. 1. (PARTS PER MILLION.)

Total solids.....	54.0
Free ammonia.....	0.06
Albuminoid ammonia.....	0.094
Nitrates.....	0.00
Nitrites, nitrogen in.....	0.000
Chlorine.....	0.00
Alkalinity.....	1.25

Samples of rain water have been taken that were slightly acid, but usually this is nearly neutral.

Analysis of wet snow that fell the evening of November 4, 1910, at practically the same point as that where No. 1 was taken:

### (PARTS PER MILLION.)

Total solids.....	24.0
Loss on ignition.....	10.0
Free ammonia.....	0.020
Albuminoid ammonia.....	0.025
Nitrates, nitrogen in.....	0.005
Nitrites, nitrogen in.....	0.006
Chlorine.....	trace
Calcium oxide.....	3.6
Magnesium oxide.....	0.00
Alkalinity.....	8.00

Many industries demand rain or distilled water. If the natural product were collected and appropriated to power use, every thirty-six acres area would offer ample supply for a one thousand boiler horsepower plant, running continuously throughout the year and using the water but once; condensing water not considered. If made slightly alkaline, this would be ideal for power use.

Not until this free gift of nature has become hard and soiled do we attempt to use it. As the power house needs water in large quantities, any difficulty in this direction is felt at once severely.

Among the thousands of manufacturers, the larger percentage accept water as delivered and make the best of it, while a constantly increasing number place the matter in the hands of competent specialists who make recommendations resulting in economy. With the increasing use of resident chemists in manufacturing concerns, the water problem should be simplified and the water improved. The steam turbine, returning 65 per cent. of oil-free exhaust steam, is sure to produce great economy where water is expensive, but a manufacturing plant needs clean soft water for a variety of purposes and in such quantity that every commercial chemist should familiarize himself with the elements at least of the art.

For such, I can offer no better methods of analysis than those adopted by the Pittsburgh Testing Laboratory and splendidly described by Dr. James O. Handy.<sup>1</sup> For practical water purification, analyses made by this method leave nothing to be desired either regarding the quality of the water obtained or the quantity of lime and soda required.

In my own laboratory, the methods indicated by Mr. Handy are carried out as follows:

Fifty cc. of water are floated in a water bath in a weighed platinum dish. The dried residue is placed in a desiccator one hour and weighed. The difference between the first and second weights is termed "total solids." The phenolsulphonic acid method is applied to this residue for nitrates.

Two hundred and fifty cc. of the water are evaporated to dryness in a glass dish; also floated in the water bath. To the residue freshly distilled water is added. A policeman is used to free the sides of the dish from encrusting salts. The whole is warmed and filtered. The filtrate is saved for soluble calcium and magnesium. The precipitated carbonates of lime and magnesium are washed with the least possible amount of water until sulphates and chlorides disappear from the filtrate. The funnel with the precipitate is removed to another flask, filled with distilled water, and a few drops of hydrochloric acid are added. The whole is washed into the flask below. One of the last drops is used to carry a drop of methyl orange solution. Ammonia is now added to the filtrate to neutral reaction. About five grams of ammonium chloride are next added. When this has dissolved oxalate of ammonia is added, in excess. This solution is boiled for twenty minutes, cooled, filtered and washed with 150 cc. of hot distilled water. A few crystals of dry oxalate of ammonia are added to the filtrate to make sure of complete precipitation. Two hundred cc. of distilled water are placed in a flask. Five cc. of concentrated sulphuric acid are added. Liquid is heated to boiling. Permanganate is added to a slight pink. The filter paper containing the lime is now added to the flask. A slight rotational movement is given and the whole is titrated with permanganate until the first pink color is matched. If a smaller quantity of water is used, the filter paper is liable to be oxidized. Magnesium is estimated as pyrophosphate with the precaution that the filter paper is moistened with ammonia solution before filtering process is begun. The lime and magnesium in the neutral soluble filtrate are estimated in a similar way. One hundred cc. of water are titrated with standard silver nitrate solution, using 10 cc. of Mason neutral potassium chromate as an indicator. A blank is run with distilled water and the result obtained subtracted from the first. With waters high in carbon-

ates or heavily charged with other mineral matter, I never feel sure of a volumetric chlorine determination. Wherever accurate work is demanded the gravimetric method is far superior and takes but little additional time relatively. Sulphur trioxide is estimated in 100 cc. of water made slightly acid with hydrochloric acid at the outset and boiled until at least half the liquid is expelled. One liter of the water is evaporated to dryness with a few drops of hydrochloric acid. The residue is taken up with distilled water and filtered. The silica is estimated from loss when the ignited and weighed precipitate is treated with hydrofluoric acid. The oxides of iron and aluminum are precipitated in the filtrate from this residue, washed and weighed.

Alkalinity and hardness tests are made to check other results. With very hard waters, I suggest the use of not more than 10 cc. made up to 100 with distilled water for determining hardness.

It must be remembered that carbonates are slightly soluble in water. The inaccuracy can be confined between two and five parts per million by using proper precautions. Total ammonia tests should be made with all colored waters. Organic matter may cause severe corrosion in a boiler. For practical purposes the lime, magnesium, chlorine, nitrate, sulphate and ammonia tests are sufficient. The methods of combination are so generally known as not to require repetition. Water analysis is now an exact process, and uniform results can be obtained if care is used. As a check against the results previously obtained, I test 100 cc. of raw water for total calcium and magnesium. If these results vary from the sum of soluble or insoluble lime or of soluble or insoluble magnesium as much as five parts per million, the determination is made again. All water analyses should be checked by the method of Lunge, Vol. I, part 2, page 765. With such an analysis we are prepared to treat one liter of water.

Determine the lime and soda required. Make solutions, the strength of which is accurately known. Add these in quantities representing the salts demanded. Agitate the flask and set aside for at least four hours. Now filter and treat the filtrate as a new sample of water, making a complete analysis. Examine for excess soda and lime water. Once satisfied with the proportioning of the chemicals, try a barrel lot, and stir with a paddle or use such a device as shown in cut below, which can be gotten up for about \$25.

The laboratory difficulties of water purification are few. In the boiler house these multiply. Although the application of a very old discovery, the lime-soda process is far from ideal. Not until the lime and magnesium salts are removed without the consequent introduction of sulphate of soda can the art be said to be approaching perfection. Unfortunately we

<sup>1</sup> *Engineering News*, May 26, 1904, pp. 500-8.

are unable to employ anything else so cheap for the purpose.

Every water softening installation must be treated

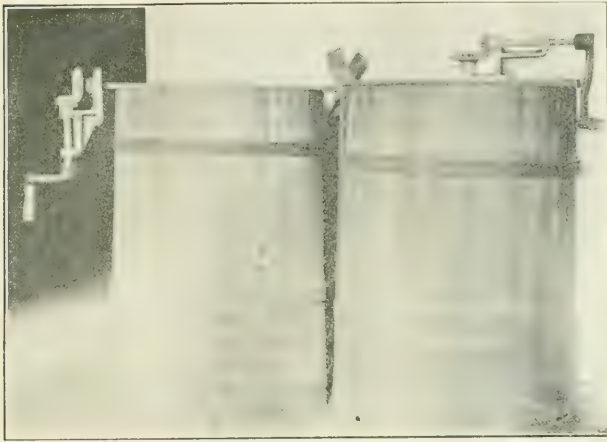


Fig 1 Sample mining tanks

as a separate study. Owing to this fact, it is very difficult to get up a machine or apparatus for general sale as in the case of a heater or pump. The quality of the water may vary rapidly from day to day or from month to month; the boilers may be provided with water inlets at unusual places; the piping may be peculiar or the returns may at times contain large quantities of oil. To these add engineers and firemen who are positive that water purification plants are unnecessary and a constant bother, and one is able to see that the installation of a machine or apparatus under these circumstances may be accompanied by uncertain results. If given proper attention, a well designed water softening plant may be of great value to a manufacturer, provided the water has a hardness greater than 60 parts per million.

In preparation for any change in the water supply of a large plant, samples should be placed in the hands of a competent chemist at least one year in advance. Monthly analyses should be made with a full report. Having determined the quantity and quality of water available, tenders for the plant can be gotten up. This is the only fair way to prepare the contractors for proposals in connection with such a difficult subject.

I offer no criticisms regarding blank proposals usually sent out, excepting that many waters foam seriously if fully softened. A 90 per cent. removal of scale-forming salts is rarely necessary for practical purposes and is not desirable for boiler use. The scale building power of gypsum is often completely broken down when 50 per cent. is removed. The daily operating cost is thus much reduced.

Although water softening is a chemical process, machines and apparatus are required to incorporate the chemical with the water to separate any undissolved salts that may form or precipitate, if more than one hundred gallons of water are required per hour.

The question of the time required for complete softening both cold and hot and the precipitation of the salts formed are subjects that can be fully decided before an expensive machine is ordered or built.

There are two distinct classes of water purifying apparatus, the intermittent and the continuous. The continuous process may further be subdivided into apparatus that conforms to a varying draught of water and to another form that runs at a uniform rate but only when water is required for the supply tank.

For the benefit of chemists who may read this article, I suggest certain forms of apparatus that have been installed, applicable to the softening of water from a few hundred gallons to two hundred thousand gallons per day.

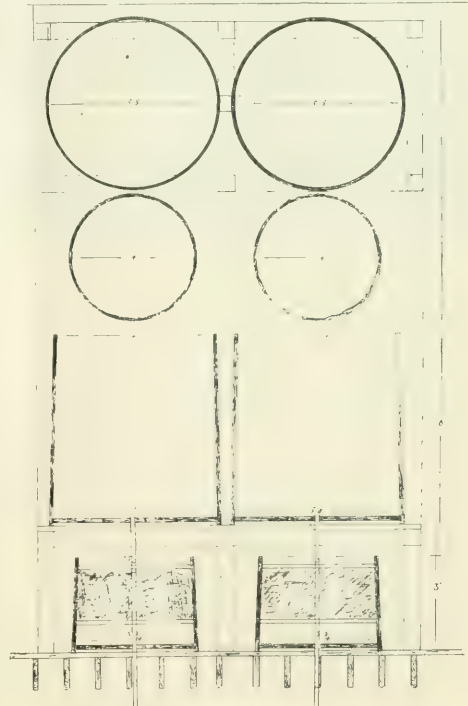


Fig 2 Intermittent process, 2000 gals.



At a certain coal trestle a 35 h. p. engine is used. It was found very difficult to keep the boiler in good condition and a softening device was called for. A 1000-gallon cypress tank was made and placed on the platform above the boiler and a second tank, provided with an excelsior filter, was placed so that



Fig. 3—Fraction tank.

the top of the filter bed was a little below the bottom of the first tank. The larger tank is filled with water. The chemicals are mixed in a pail of water and added slowly. A long paddle is used to mix these thoroughly. After four hours this water is drawn through the filter. This proves very efficient and the boiler has been kept clean for several months. This is practically one-half of the plant shown in Fig. 2.

The simplest agent for mixing purposes is air. This is best applied by an aspirator or a compression pump. I have built and installed a two thousand-gallon plant equipped with such an arrangement. Where the water supply enters the tank at the top (Fig. 2) a T is placed instead of an elbow. This T carries an upright pipe about three feet long open at the upper end. The water supply enters at a downward angle of about  $45^\circ$ , dragging air from the open pipe to the bottom of the tank. The attempt of this confined air to rise thoroughly stirs the liquid and any suspended solids as lime and soda. By adding the chemical slowly after the bottom of the tank has been covered with water, a thorough mixing takes place. The filter for such a simple system is built up of about eighteen inches of closely packed willow or poplar excelsior and finally covered with unbleached cotton cloth held in place by means of wooden lattice work.

Such an apparatus in duplicate, softening one thousand gallons in each tank at a time, costs about \$250, including pipe, valves and suitable sludge outlets. Intermittent softening can in this way be made very effective. A small power plant can be handled by this apparatus—100 horse power is not too large. It is to be remembered that the chemicals require about four hours sedimentation.

For a 250 horse power boiler plant a more expensive apparatus was designed. The space available was an area  $9 \times 19$  feet between the boiler house, stack and factory proper. Any considerable altitude was prohibited by the necessity of light for machinery in the factory. Accordingly, the ground was excavated above seven feet to shale rock, ample drainage being provided at this depth. A three-compartment tank was then built of brick laid in concrete and concrete-lined, the rear tank being 11 feet in height and the others ten feet. This design was adopted to give the water sufficient time for complete sedimentation. The necessary lime and soda ash tanks were placed immediately above the mixing tank and filter bed, respectively. Sewer tiles were

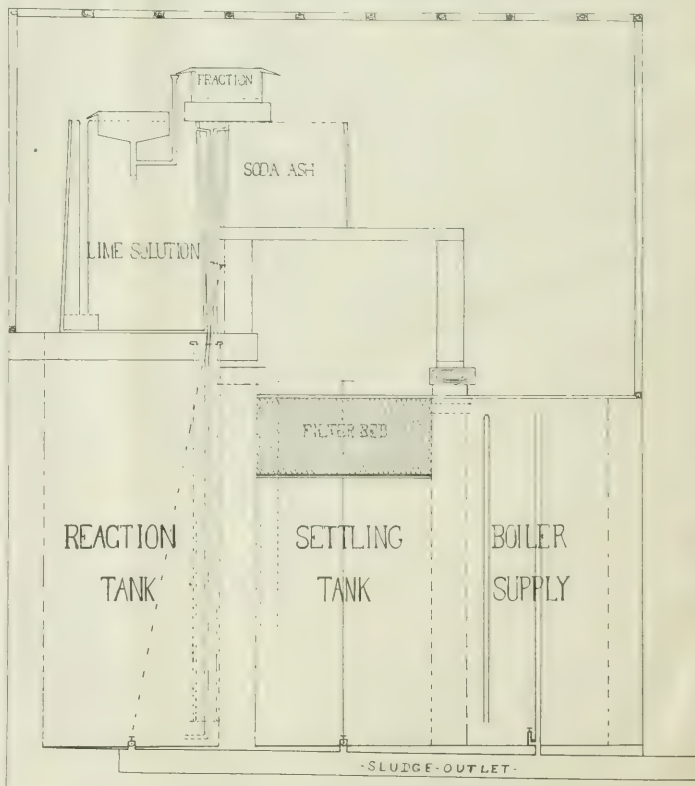


Fig. 4.—Section 250 H. P. plant.

used as conductors wherever practicable, no valves being necessary between the water inlet and sludge outlets. Those placed at the bottom of the large tanks lead into an eight-inch sewer tile drain which in turn opens into a sludge basin of brick and concrete.

Water enters the fraction tank (Fig. 3) and flows in three streams to the soda ash tank, the lime-mixing tank and the mixing tank proper. A float in the supply tank operates a quick-closing valve over the fraction tank.

The smallest stream of water passes into an iron supply tank provided with a partition extending nearly to the bottom. The water enters the larger compartment where the chemical is also placed and dissolved by steam. Raw water entering this tank rides on the top of the heavier soda solution and drives it under the partition and out over the top of the smaller compartment, where it mixes with the main stream.

The second water fraction flows directly to the bottom of the lime basket coming up through the particles of lime and then flowing to the bottom of the large lime-water tank, from thence to the main stream, where it mixes with the raw water and soda solution. The chemicals and water flow through a twelve-inch vertical tile pipe to a point about one foot from the bottom of the concrete tank where the entire mixture spreads out. The air bubbles start upward and thoroughly mix the entire mass. From this tank the water and sludge pass to the bottom of the filter apartment. The filter bed is of excelsior, twenty-four inches in thickness and has to be changed twice per year. Fifty square feet of filtering surface will take care of one thousand horse power unless very unusual draughts of water are demanded. This plant costs complete about \$800. The following analysis shows the nature of the water both in a raw and purified state:

	Parts per million.	
	Raw.	Purified.
Calcium carbonate.....	161.0	28.0
Calcium sulphate.....	421.0	0.0
Magnesium carbonate.....	0.0	Mg(OH) <sub>2</sub> 27.87
Magnesium sulphate.....	98.0	0.0
Calcium chloride.....	0.0	0.0
Magnesium chloride.....	0.0	0.0
Sodium sulphate.....	0.0	556.0

This plant was started by the engineer in charge with an efficiency of 75 per cent. This has been increased to 90 per cent. and can be maintained at this point. It has been found, however, that 75 per cent. efficiency is all that is necessary to prevent the formation of scale. The old scale of the boilers

was removed in three months. With returns, 13 pounds of soda ash and 12 pounds of lime are required to operate 200 h. p. thirteen hours, the whole cost for materials being seventeen cents. The engineer in charge spends about one-half hour per day in connection with the water softening plant. His time is occupied in opening and closing sludge valves, charging lime and soda ash and cleaning out the lime



Fig. 5.—View of 250 H. P. softening apparatus looking toward soda tank and into filter compartment.

basket. The coal consumption was lowered 25 per cent. by this installation.

In these instances, power mixing was not necessary. Where, however, the water is hard and the horse power is five hundred or above, some form of stirring apparatus should accompany any water purifying plant.

Something over a year ago a thousand h. p. plant was installed where the water was taken from a deep well with a very uniform hardness, 14° Clark. The usual concrete tanks were built. The lime mixing apparatus is shown in Fig. 6.

This consists of a half cylinder within which revolves a heavy rectangular arm. Raw water flows into a weir and from thence, by three rectangular orifices, outward. The portion needed to form lime water passes into the lime stirring apparatus at one

end and overflows through a pipe at the other end, finding its way into an intermediate settling tank, falling from this into the vertical mixing column.

The portion of raw water required for soda solution passes to a slow pump (Fig. 7) which consists of two vertical cylinders concentric with two larger

steel tanks. Raw water flowing into the left-hand outer tank pushes the corresponding cylinder upward, lowering the right-hand cylinder and driving out soda ash solution in proportion to the raw water entering at the other side. Steam keeps this soda ash in a heated condition. The lime saturator is

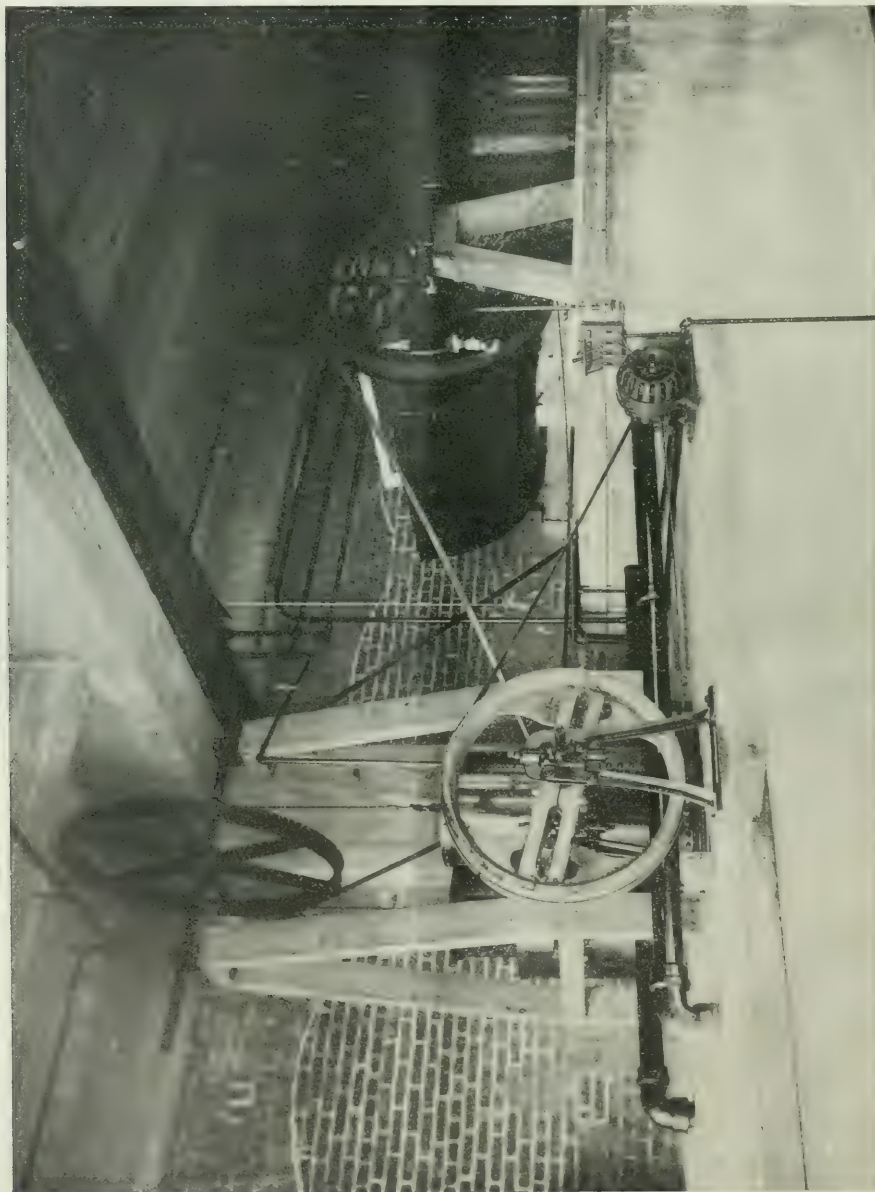


Fig. 6.—1000 H. P. plant.



driven by a 1 h. p. motor, which is run continuously. Although the amount of water used varies constantly, the quantity of lime and soda ash remains in very

both running under full head from the time the float trips the Cutler-Hammer device until it is again opened by the return of the float to its former position. This is the most satisfactory power arrangement that I have used, as the electric current is only required when water is needed.

## ANALYSIS OF WATER BEFORE AND AFTER TREATMENT

	(Parts per million.)	
	Raw.	Treated.
Calcium carbonate	162.50	Sulphate
Calcium sulphate	475.00	hardness re-
Magnesium carbonate	6.00	moved. Alka-
Magnesium sulphate	216.7	linity held at
Sodium chloride	28.8	170.

The lime-soda process has been successfully employed in boiler plants and in private residences where the water was saturated with gypsum, containing about 1600 parts per million, with 170 to 200 parts of calcium and magnesium carbonate per million. From boilers the sulphate of soda ormed must be blown out often, otherwise serious foaming results. To treat hard water uniformly, so that it will neither scale or foam, is the aim of the successful specialist.

Manufacturers are ready to accept the suggestions of their chemists if these are practical. As shown in the foregoing article, fifty gallons of water can be softened to show what such a process will do for the dyer, tanner, laundryman or the power plant. Engineers generally understand what can be done when you interpret your results by stating, for instance, that raw water containing twenty-five grains of hardness per gallon has been reduced to one containing but four.

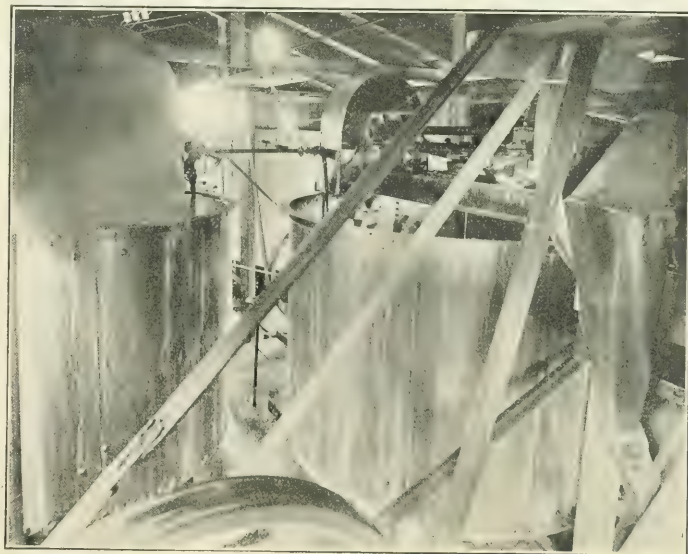
exact proportion to the water used. The following is a series of analyses taken at different times during the past year:

	(Parts per million.)				
	Sept.	Sept.	Oct.	May	
Raw.	10, '09.	30, '09.	10, '09.	25, '10	
CaO.....	141	13	17.4	19	10.4
MgO.....	27	17	9.4	16	14.5

As shown by analysis, this water is kept nearly in a neutral condition. This form of saturator could be improved by raising the boiler plate about eighteen inches above its present height. However, it answers every purpose for the continuous and complete formation of lime water; of course with some milk of lime. By increasing the height and placing a porous partition over the stirring apparatus, clear lime water could probably be delivered.

Last spring a 1500 h. p. plant was required in a very hard water section. 250 pounds of chemicals had to be charged at a time for the day's run. This required a very substantial lime saturator. Accordingly, a steel tank stirring and proportioning apparatus were designed in one. This very thoroughly mixes the chemicals which are added together and are stirred constantly during the entire day. This apparatus is shown in Fig. 8.

This plant is driven by electricity at a uniform rate with alternating current motor. A valve in the boiler supply tank controls water and electricity,



Patent applied for.

Fig. 8. Stirring apparatus.

The improvements in the art must come from the men equipped with chemical knowledge. I have been unable to discover a mechanical process that will fully separate encrusting salts from water inexpensively. Closed heaters separate a certain percentage of carbonates depending on the temperature, pressure and relative flow of the water. I

## HEAT TREATMENT OF HIGH-SPEED TOOLS.<sup>1</sup>

By C. P. BERG, M. W. S. E.

Received November 1, 1910.

The experiments described in this paper were undertaken in order to obtain the relation between temperature in tempering and the life of tools to a greater degree of exactness than heretofore known to the writer.

The perfection of the electric furnace for high temperatures and development of same into dimensions for such practical purposes as heat treatment of metal-cutting tools, in connection with the electric pyrometer for measuring these high temperatures, has made possible such investigations as stated above.

The writer will confine himself conclusively to the attempt of solving the problem as it concerns the effect of various temperatures upon the life of high-speed tools, or the comparative values of the same.

Although the carbon steels are of decidedly earlier origin and have been experimented upon by several investigators, it is the hope of the writer to attempt an addition to the present available information in the near future.

Most notable of recent scientific work in this line is the paper presented by Mr. George W. Sargent, Ph.D.,<sup>1</sup> at the meeting of the Franklin Institute, June 3, 1909: "Some remarks upon the critical points of steel, their method of determination, and the value of same," in which he records a series of experiments made at the Carpenter Steel Works.

While the heat treatments and various tests described in his paper were conducted in a thoroughly scientific manner, Mr. Sargent failed to show the value of his investigations on the life of metal-cutting tools.

Fully appreciating the value of specialists for the various tests required to complete this work, the writer has been fortunate in being associated with, and assisted by, professional experts during the entire experimenting period, each one carrying on his special part of the investigation.

The writer would particularly mention Messrs. W. C. Post, A. D. de Pierrefeu and J. H. Critchett, of the Chicago Metallurgical Laboratory, in connection with the metallurgical examination by photomicrographs, Mr. James Lowrie, Ph.D., with the hardness test, and Mr. W. V. Young, of the Hoskins Mfg. Co. He would also acknowledge his indebtedness to the Hoskins Mfg. Co. for enabling him to carry on the heat treatments at their Chicago demonstrating



Fig. 9.—Housing for 2000 H. P. plant, 12' x 40'.

have found a removal of from 25 per cent. to 75 per cent. of these salts. High temperature and pressure heaters made to remove gypsum fail fully to do so. Analyses of treated water from such heaters have not shown more than 50 per cent. to 75 per cent. removal of sulphates. Moreover, the process is expensive both from the standpoint of steam used and labor required to remove the trays encrusted with heavy scale.

A considerable percentage of the soft returned water from a plant can be saved and used again. Chemical engineers need to thoroughly investigate the removal of oil from water. It seems possible to perfect a device provided with a chemical bath that will effect complete removal of oil. We need a thorough investigation of chemicals or processes that shall result in the complete removal of sulphates from water. Barium salts are considered dangerous by concerns using live steam for food purposes. Whether, when foaming occurs, such salts are dangerous is yet to be determined, but it seems entirely possible that the prejudices are fully founded. No cheaper material than lime can probably be found for the removal of carbonates.

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plant, and the Link-Belt Company, at which shops the cutting tests were performed.

To recapitulate: The writer's work may be said to consist of:

A. Establishing a guide as to how rapidly the steel should be heated under the high heat treatment by a heat absorption test.

B. Determining at which degree of temperature in the heat treatment, the maximum cutting efficiency occurs for a steel of a certain chemical composition.

C. Giving reasons for the relations found by these tests by metallurgical examinations and to illustrate the same by photomicrographs.

*Steels Used in Test.*—Four prominent high-speed steels were selected to be experimented upon. These steels were marked A, B, C, and D, and these marks will be retained in referring to the four series of specimens undergoing the various tests.

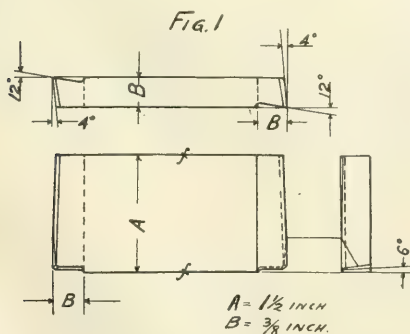
The chemical analyses of these steels are as shown in Table I:

TABLE I.—CHEMICAL COMPOSITION OF STEELS.  
Figures are percentages.

	A.	B.	C.	D.
Carbon, C.....	0.70	0.56	0.74	0.67
Silicon, Si.....	0.211	0.248	0.262	0.278
Sulphur, S.....	0.016	0.035	0.016	0.010
Phosphorus, P.....	0.010	0.012	0.016	0.015
Manganese, Mn.....	0.27	0.20	0.21	0.22
Chromium, Cr.....	4.76	5.54	5.80	3.30
Tungsten, W.....	15.15	8.45	10.94	15.37
Nitrogen, N.....	0.005	0.005	0.004	0.015

*Tools Used in Test.*—In order to eliminate the effect of forging upon the steels to be tested, straight tools for boring or inside turning, ground to shape and to standard angles in a grinder, were decided upon.

Steel bars of  $\frac{3}{8}$  by  $1\frac{1}{2}$  in. size were cut off from the four previously mentioned steels, to be made into tools for roughing cuts in boring cylinders to  $4\frac{1}{2}$  in. diameter. The tools were treated and ground with a cutting edge on both ends and to cutting angles as shown in the accompanying sketch (Fig. 1).



Boring tool used in tests.

*Specimens Used for Physical Tests.*—Cylinders made from cast-iron of a chemical composition producing

exceptionally hard castings were provided for this test.

In order to insure equality, the greatest care was taken in preparing the molds for these castings, and all were poured from the same heat.

In view of the fact that the life of a tool decreases with the increase of combined carbon in the castings on which it is used, and again that the amount of combined carbon is dependent upon the rapidity with which the cast-iron is cooled after pouring it into the mold, it became necessary to find some method by which these castings could be cooled in the same length of time.

The molds were therefore specially arranged for this purpose, and eight minutes after the iron was poured the cores were removed and the castings cooled in water. This gave the castings as nearly as possible the same amount of combined carbon.

Dimensions of the cylinders were as follows: Outside diameter, 8 inches; length, 8 inches; and diameter of core, 4 inches; leaving  $\frac{1}{2}$  inch of metal to be removed by the double end tools to be tested, or, in other words, providing for  $\frac{1}{4}$ -inch depth of cut for each end of the tool.

The thickness of metal or walls of the cylinders being 2 inches, the castings were inspected for soundness and then considered if of the quality for the test or condemned.

*Heat Treatment of the Tools.*—The temperatures used in the heat treatment of tools have heretofore generally been measured in practice by the terms: cherry-red, bright yellow, white, etc. These measurements of heat were probably as correct as any other in connection with the old-time method of tempering tools in the blacksmith forge, where no accurate control of the heat could be obtained.

Admitting that there are experts in this line, who are able to guess temperatures very closely by the color of the heated steel, the writer has heard differences of opinions, when the limit line was to be drawn between white and bright yellow, etc.

With the modern electric furnace, its perfect control, evenly distributed heat, reducing atmosphere preventing burning of the steel, and the thermoelectric pyrometer for measuring temperatures, the science of treating metal-cutting tools has taken a long step forward.

The instruments as used for the experimental tools are shown in the accompanying illustration (Fig. 2) from a photograph. To the left can be seen the muffle furnace used for preheating the steel slowly up to 1400° F., prior to transferring it to the tube furnace, seen to the right in the picture, there to be subjected to the high heat treatment.

The muffle furnace, to the left, is of the wire resistance type constructed for temperatures up to 1800° F.

The tube chamber design of furnace, to the right,

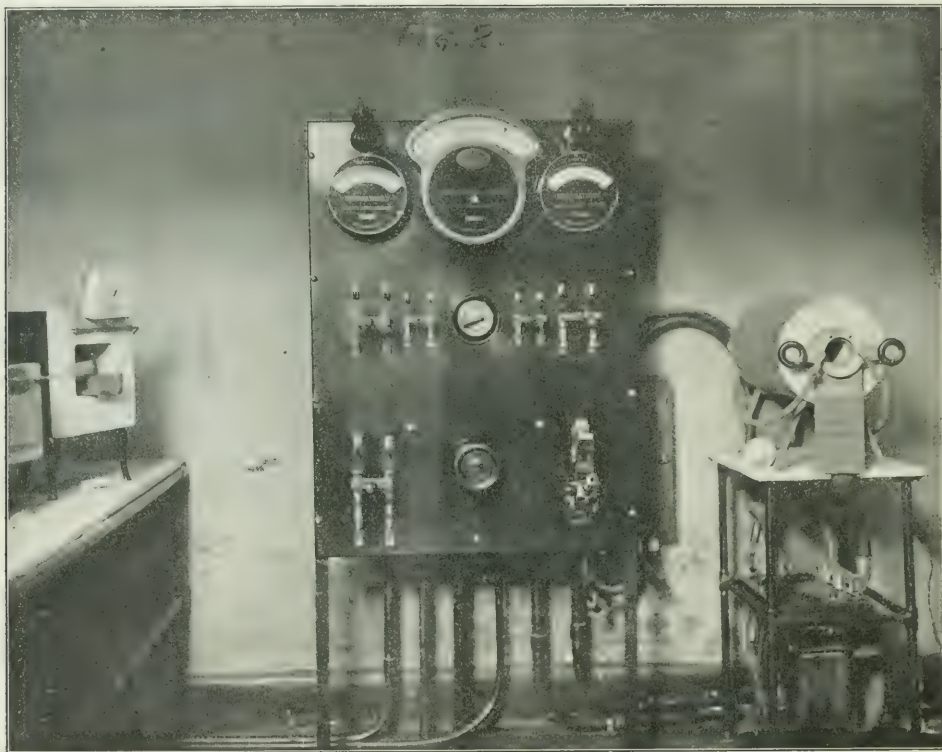


where the experimental tools were subjected to the high-heat treatment, is constructed for temperatures up to 2600° F.

The current for both of these furnaces is controlled on the switchboard shown in the center of Fig. 2.

allowed for the heat to penetrate thoroughly to the center of the tool, which otherwise would be in danger of cracking.

To do this it is necessary to know the length of time required by the tool under treatment to absorb



Electric heating furnaces and switchboard

The switchboard also carries the thermoelectric pyrometer, which is connected with the thermo-couples by the switch in the center of the board, this rendering possible the reading of temperatures in several furnaces on this one instrument by turning the switch, the contact points of the switch being numbered to avoid confusion. A wiring diagram of the pyrometer and selective switch is shown in Fig. 3.

To insure accuracy the thermo-couples used were calibrated before and after the readings made on the temperatures of the test specimens. The calibrating consisted in taking a reading on water at the boiling point (212° F.), on aluminum at the melting point (1215° F.), and on copper at the melting point (1949° F.).

In giving high-speed tools the high-heat treatment, the temperature should be raised rapidly to the desired degree for quenching, but enough time should be

the heat to which it is subjected. In order to ascertain this for a guide in treating the experimental tools, the heat absorption test was made, from which the results are shown by the diagram in Fig. 4.

Four pieces of steel of equal size,  $\frac{3}{8}$  in. by  $1\frac{1}{2}$  in. by  $1\frac{1}{2}$  in., one from each end of A, B, C, and D, were prepared with a hole to receive the end of the thermo-couple, as shown in Fig. 5.

The furnace was run up to 2200° F. and kept at this temperature. The test pieces were placed in the furnace individually and time observations were taken on the increasing temperature of the steel.

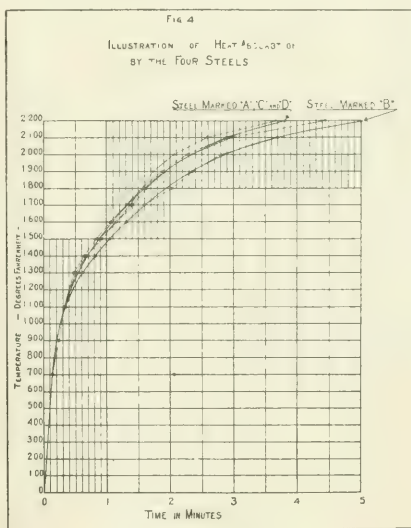
Noting the uniformity of the curves in the diagram, Fig. 4, it will be seen that the molecular change in the steel up to 2200° F. did not at any point disturb the evenly increasing temperature of the specimen. As will appear later, it was found that some of these steels are treated with the best results at

2150° F. The molecular change evidently is not violent enough and quick enough to stop the increase of temperature in the steel, at least it could not be observed by the instruments used.

From other tests made on heat absorption with various sizes of steel, it appears that the time for the absorption of heat increases very nearly in proportion to the thickness of the steel. Thus, a piece of steel  $\frac{3}{4}$  in. thick requires twice as long a time as is shown by the diagram in Fig. 4, which would be 6.6 minutes for a temperature of 2150° F., for any one of the A, B, C and D steels.

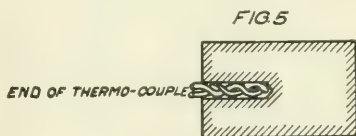
Plate I shows fractures of specimens from Series A, which have been heated to 2150° F. but which were

the necessity of careful observation in the matter of time for the tool to remain in the furnace to become thoroughly and uniformly heated.



The heat absorption of steels.

A hardness test of these specimens performed with a scleroscope gave the results shown in the following table:

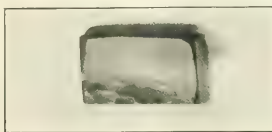


left in the furnace a certain length of time after reaching this temperature before quenching in oil at 100° F. Comparing these fractures with the ones from the experimental tools and the results from the physical tests of the latter, they strongly indicate

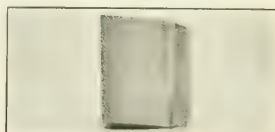
Fractures from specimens of Series A heated to 2150° Fahr. and the length of time for the specimens to remain in the furnace varied. Specimens quenched in oil at 100° Fahr.



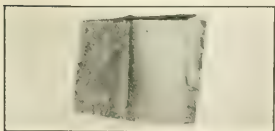
1—Left in furnace 2 min. before quenching.



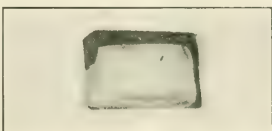
2—Left in furnace 4 min. before quenching.



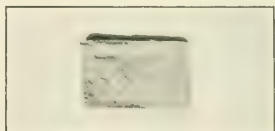
3—Left in furnace 6 min. before quenching.



4—Left in furnace 8 min. before quenching.

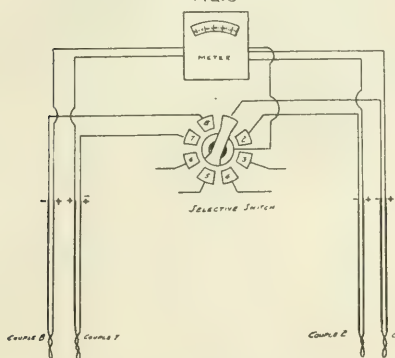


5—Left in furnace 10 min. before quenching.



6—Left in furnace 12 min. before quenching.

FIG. 3



Electric pyrometer.

TABLE II.

Specimen.	Length of time left in furnace. Minutes.	Hardness by scleroscope.
1.....	2	80
2.....	4	79
3.....	6	78
4.....	8	68
5.....	10	79
6.....	12	70

Based upon the above results, the heat treatment of the experimental tools was undertaken.

The specimens were marked, preheated to 1400° F., and from this temperature heated to the various degrees of high heat, as shown in Table III. At the temperatures indicated in the table, the specimens were quenched in oil, which was kept constant at 100° F.

For convenient comparison, the results of hardness tests with the scleroscope upon the treated specimen have been shown in Table III:

TABLE III.

A.....	1	1850	78
	2	1900	81
	3	1950	76
	4	2000	78
	5	2050	81
	6	2100	82
	7	2150	83
	8	2200	81
	9	2250	77
	10	2250	77
B.....	0	2300	74
	11	1850	78
	12	1900	74
	13	1950	75
	14	2000	77
	15	2050	83
	16	2100	83
	17	2150	82
	18	2200	79
	19	2250	78
C.....	20	1750	68
	21	1950	78
	22	2050	80
	23	2100	80
	24	2150	83
	25	2200	80
	26	2250	75
	27	2300	73
	28	2350	-
	29	2325	71
D.....	30	2350	65
	31	1950	70
	32	2050	75
	33	2100	76
	34	2150	81
	35	2200	79
	36	2250	83
	37	2300	86
	38	2350	86
	39	2300	86
	40	2400	84

Specimen 0, of Series A, softened and caved in on one side.

Specimen 28, of Series C, softened so the free end (not supported by the tongs) tore off in removing it from the furnace. Specimen 30 was taken to replace the broken one, and special precautions were made for its removal from the furnace, and it was quenched without mishaps.

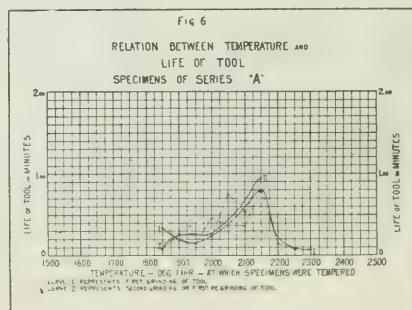
The specimens receiving the maximum heat all fused at the ends without exception, and some were, as previously stated, considerably softened.

In order to get the reading of temperature of the steel itself, a wire loop (wire  $\frac{3}{64}$  in. diam.) was put around one end of two specimens, which were to receive an equal amount of heat. The loop was made loose enough to permit the moving apart of the two free ends of the specimens. A wedge-formed space was obtained between them, in which the end of the thermo-couple was held firmly, yet from which it could be easily removed.

*Physical Tests.*—The life or durability of these tools, treated in the previously described manner, appears to vary a good deal. Being ground into tools as described in preceding paragraph, and shown in Fig. 1, the specimens were put to work under equal conditions on the casting described in several preceding paragraphs.

A 34-in. vertical boring mill was selected for the test, in order that the chips should clear away from the tool easily. The ends of the cylinders were faced, to eliminate the scraping of this scale by the experimental tools.

The results from the test run on the specimens from Series A are plotted in the diagram (Fig. 6).



"A" steels—temperature and life.

It should be noted that the specimens quenched at a temperature above 2150° F. failed almost immediately and broke.

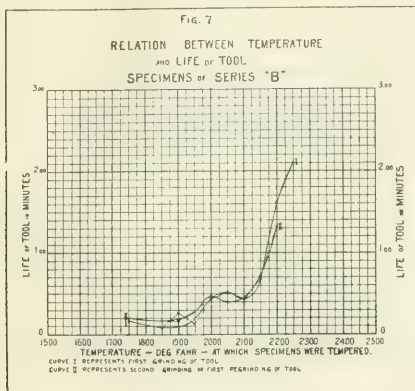
The second curve (II), which represents the second grinding of the tool, shows a slight increase in durability. This indicates the effect a second heat treatment (drawing the temper of the tool after the high-heat treatment) would have upon the tool, which effect can be gotten as readily by running the tool at high-cutting speeds until it fails, and have it reground, as by drawing the temper in the furnace. However, this method is less accurate, as there is no means of determining the heat thus developed under the cutting action, at the present time.

The cutting speed, 80 feet per minute, the thickness



of the shaving or feed per revolution, 0.0339 inch, and depth of cut,  $\frac{1}{4}$  inch at each end of the tool, were kept constant for all specimens and for both grindings.

Results from the test run on the specimens of series B are plotted in diagram (Fig. 7).



"B" steels—temperature and life

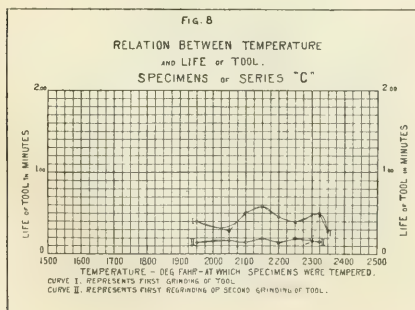
The curves here do not present a great deal of uniformity at the low temperatures, but improve and become more distinct as the temperature increases.

The specimen receiving the highest heat showed the maximum durability, but it failed very suddenly and broke into several pieces. The fractures gave evidence of brittleness.

Practically no difference in durability appears between the first and second grinding of the tool.

The cutting speed, 80 feet per minute, the thickness of the shaving or feed per revolution, 0.0339 inch, and depth of cut,  $\frac{1}{4}$  inch at each end of the tool, were kept constant for all specimens and for both grindings.

The results from the tests run on the specimens of series C are found plotted in the diagram (Fig. 8).



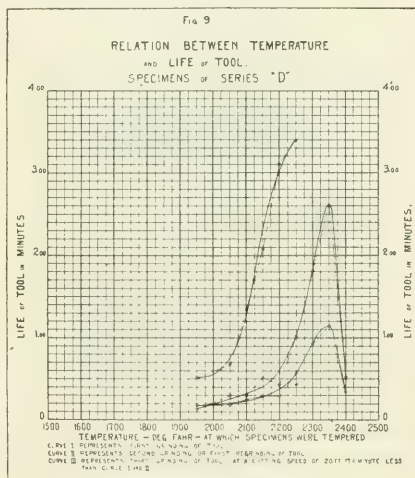
"C" steels—temperature and life.

The cutting speeds were evidently too high for this grade of steel. The durability being very low at all points, the variations are not distinct. However, it will be seen that the durability attains its maximum at 2150° F. in Curve I, representing the first grinding of the tool. The dotted lines show that the specimen which was quenched at 2300° F. failed and broke almost immediately after starting.

Curve II, representing the second grinding of the tool, does not show any variations whatever, and the difference between this and first grinding is negative. Both these occurrences are directly due to an increase in cutting speed of 20 feet per minute for the specimens on second grinding.

The cutting speed, 80 feet per minute for first grinding, and 100 feet per minute for second grinding, the thickness of shaving or feed per revolution, 0.0339 inch, and depth of cut,  $\frac{1}{4}$  inch at each end of the tool, were kept constant for all specimens.

Results from the tests run on the specimens of Series D are shown by the diagram in Fig. 9. In this



"D" steels—temperature and life.

diagram it may be noted that part of the specimens were subjected to a test also after being ground a third time.

All three curves (I, II, and III) show the variations very distinctly, and of exceptionally high durability, with the attained maximum at the quenching temperature of 2350° F. for both the first and the second grinding.

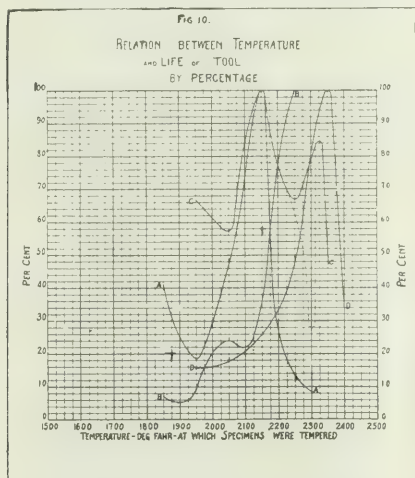
The specimen quenched at 2400° F. broke on the second grinding after failing in the length of time (0.52 minute) as shown in the diagram.

Only part of the specimens were run on the third grinding, simply for the reason that the time for

boring one cylinder would not be sufficient for the tool to fail at a cutting speed of 80 feet per minute. Cutting on more than one cylinder with the same tool would cool the cutting edge of the tool while changing and the result could not be considered.

The cutting speed, 100 feet per minute for first and second grinding, and 80 feet per minute for third grinding, the thickness of shaving or feed per revolution, 0.0339 inch, and the depth of cut,  $\frac{1}{4}$  inch at each end of the tool, were kept constant for all specimens.

In Fig. 10 is shown a diagram giving by percentage the relation between temperature and life of tool, of



The varying life of tools from temperatures.

the four series of specimens. The temperature forms the base of the diagram, and the ordinate is made into a per cent. scale.

The maximum life or durability of the tool is taken as the unit or put at 100 per cent., and the durability in percentage of the maximum can be read from the curves for any temperature used.

*Metallurgical Examination by Photomicrographs.*—In examining the photographs of the specimens from Series A, it can be seen that the size of the grain increases with the temperature at which the specimen was quenched.

Specimen No. 7, because of its size of grain, absolute freedom from separation of the constituents of the steel, and the absence of the physical defects, which appear in the specimens preceding and following this one, is the one which will be able to best withstand the vibration and rough treatment of high-speed cutting.

In specimen No. 0 the hard constituents can be seen to have separated out, forming a network around the steel crystals.

The crystals of the steel under work are forced to move around, rubbing against each other like a ball and socket joint, and this hard constituent surrounding the crystals acts in the same manner as emery in a ball and socket joint, increasing the friction and generating heat, which will rapidly destroy the tool. This specimen also shows by its physical defects and back structure (decarburized steel) that the steel was burned.

The illustrations from full-size photographs of fractures from the specimens in this series also indicate clearly the increasing size of grain with the quenching temperature of the specimen.

Examining the illustrations of the specimens from Series B, it will be seen that the grain of the steel increases gradually up to specimen No. 16, and afterwards very rapidly, showing that the steel is very sensitive to heat treatment above the temperature at which this specimen was treated.

For the same reason that specimen No. 7 was chosen as the best of Series A, specimen No. 16 is selected of this group. The physical defects which appear in the specimens preceding and following specimen No. 16 are entirely absent here.

Comparing this result with the results of the physical test shown in the diagram (Fig. 7) it appears that the two do not agree for this steel. The diagram shows the maximum durability of the Series B is attained by specimen No. 19. This occurrence can hardly be accounted for unless it is due to a minimum of separated hard constituents around the steel crystals, even at the higher temperatures.

The illustrations from full-size photographs of the fracture show the increasing grain with the quenching temperature like the steel in Series A.

The illustrations of the specimens of Series C show that the size of crystal grains in this group increase gradually up to the point where the steel becomes burned, as shown in specimen No. 30.

For the series No. 24 is chosen as the best specimen, because of its clean structure, the absence of any separation of the constituents, and the uniform size of the crystal grains.

In specimen No. 30 the steel shows the same effects of burning as specimen No. 0 of Series A, the separation of hard constituents around the crystals and the black decarburized spots.

Also in this series the illustrations from full-size photographs of fractures show the increase in size of grain with the temperature.

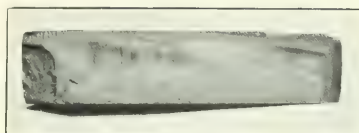
The illustrations of the specimens of Series D show a very uniform structure up to specimens No. 38 and 40.

Specimen No. 40 shows distinctly marks of being burned, by the black decarburized spots, but the hard constituents surrounding the crystals, which are found in other burned specimens, are entirely absent here.

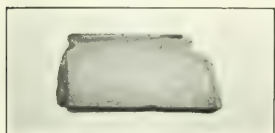
Fractures from specimens of Series A



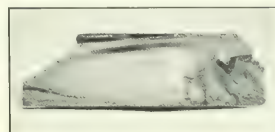
1—Quenched at 1850° Fahr.



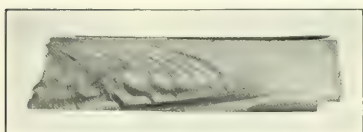
2—Quenched at 1950° Fahr.



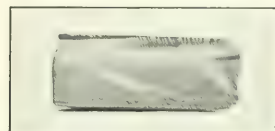
3—Quenched at 1950° Fahr.



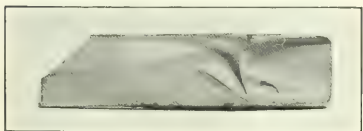
4—Quenched at 2000° Fahr.



5—Quenched at 2050° Fahr.



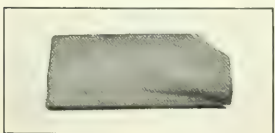
6—Quenched at 2100° Fahr.



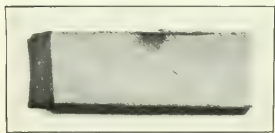
7—Quenched at 2150° Fahr.



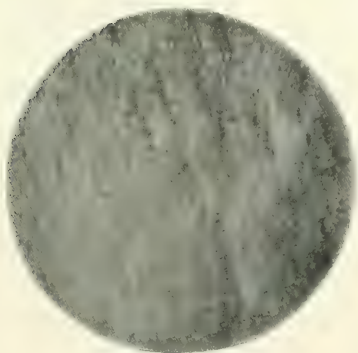
8—Quenched at 2200° Fahr.



9—Quenched at 2250° Fahr.



10—Quenched at 2250° Fahr.



No. 1



No. 4

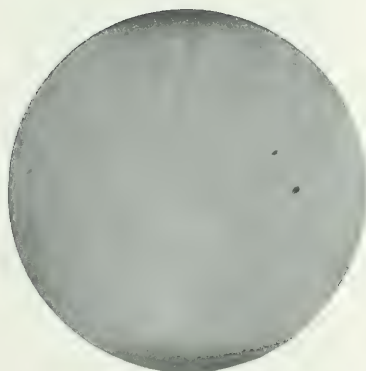




No. 5.



No. 7.



No. 8.



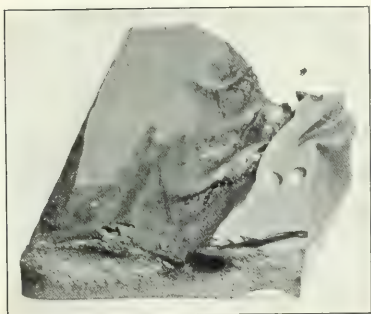
No. 8.



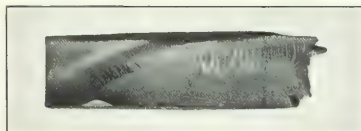
No. 9.



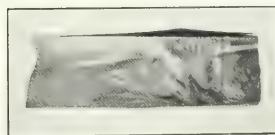
No. 0.



Series A. No. 0.



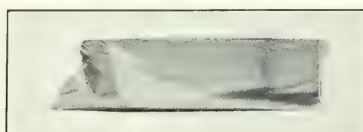
11—Quenched at 1850° Fahr.



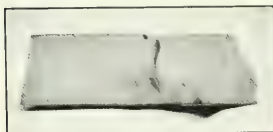
12—Quenched at 1900° Fahr.



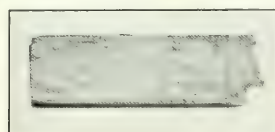
13—Quenched at 1950° Fahr.



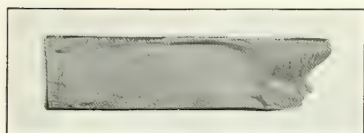
14—Quenched at 2000° Fahr.



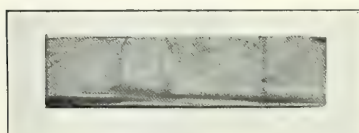
15—Quenched at 2050° Fahr.



16—Quenched at 2100° Fahr.



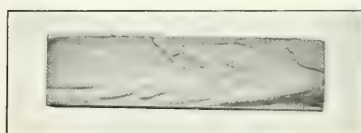
17—Quenched at 2150° Fahr.



18—Quenched at 2200° Fahr.



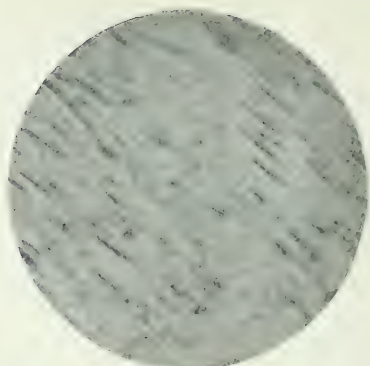
19—Quenched at 2250° Fahr.



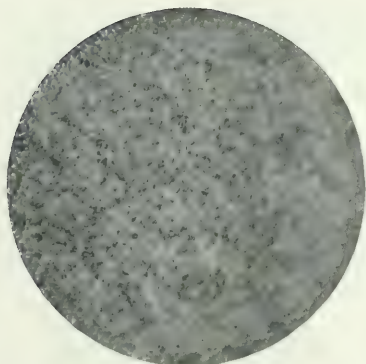
20—Quenched at 1750° Fahr.



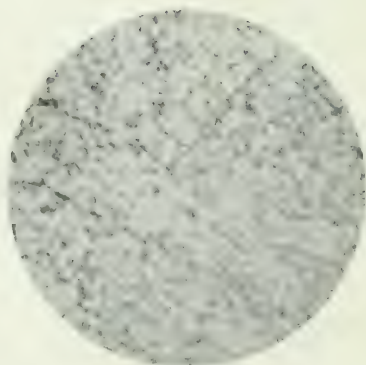
No. 11.



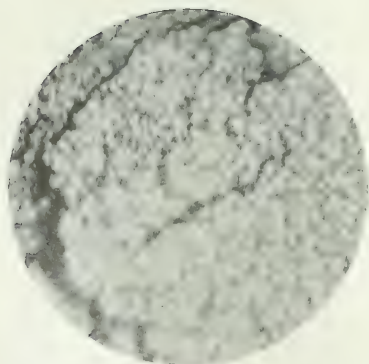
No. 14.



No. 16.



No. 18.



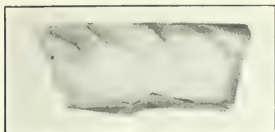
No. 18.



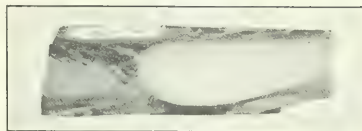
No. 19.



Fractures of specimens. Series C



21—Quenched at 1950° Fahr.



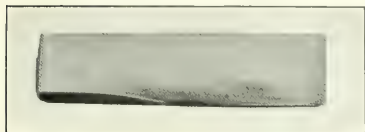
22—Quenched at 2050° Fahr.



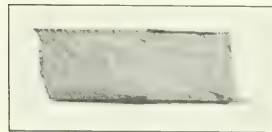
23—Quenched at 2100° Fahr.



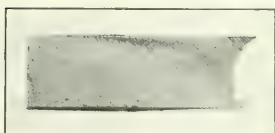
24—Quenched at 2150° Fahr.



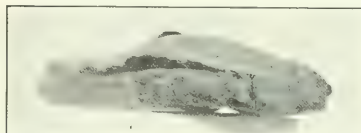
25—Quenched at 2200° Fahr.



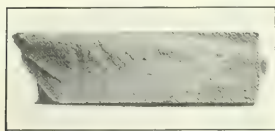
26—Quenched at 2250° Fahr.



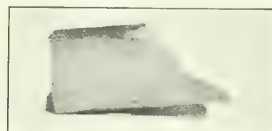
27—Quenched at 2300° Fahr.



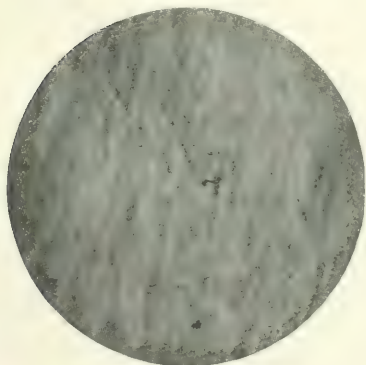
28—Quenched at 2350° Fahr.



29—Quenched at 2325° Fahr.



30—Quenched at 2350° Fahr.



Series B. No. 20.



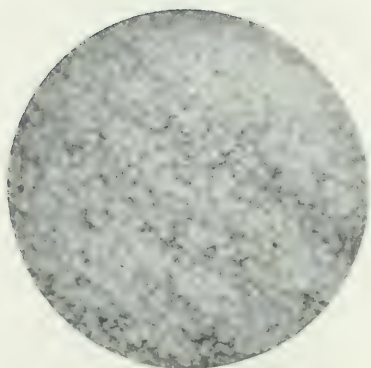
No. 21.



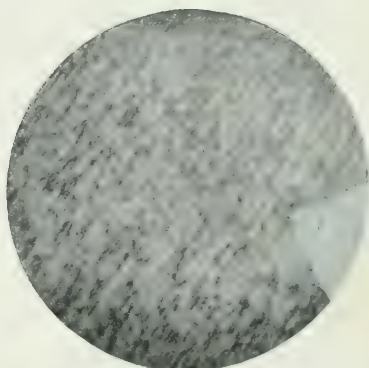
No. 23.



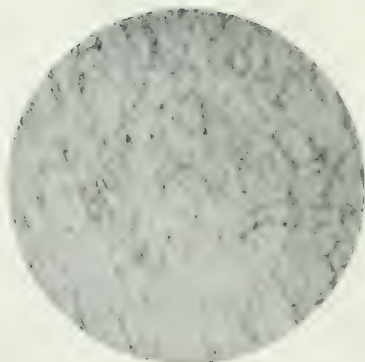
No. 24.



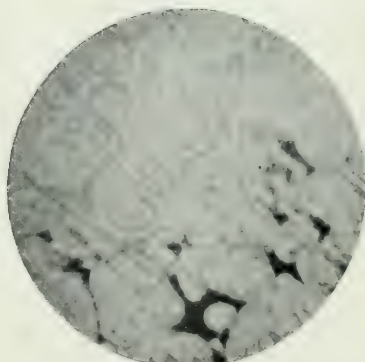
No. 26.



No. 27.

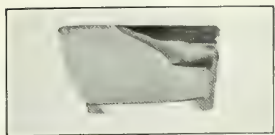


No. 29.

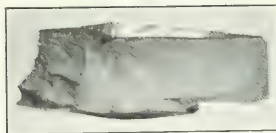


No. 30.

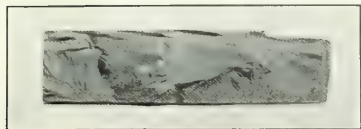
Fractures from specimens of Series D.



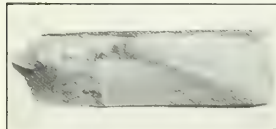
31—Quenched at 1950° Fahr.



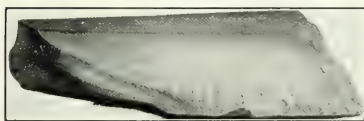
32—Quenched at 2050° Fahr.



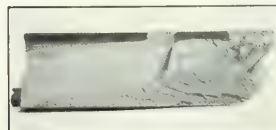
33—Quenched at 2100° Fahr.



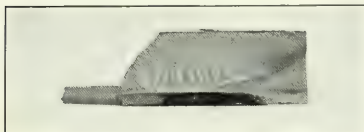
34—Quenched at 2150° Fahr.



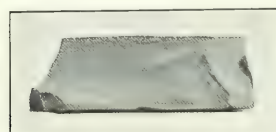
35—Quenched at 2200° Fahr.



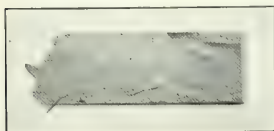
36—Quenched at 2250° Fahr.



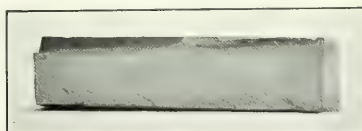
37—Quenched at 2300° Fahr.



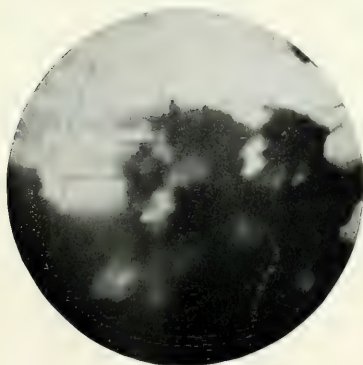
38—Quenched at 2350° Fahr.



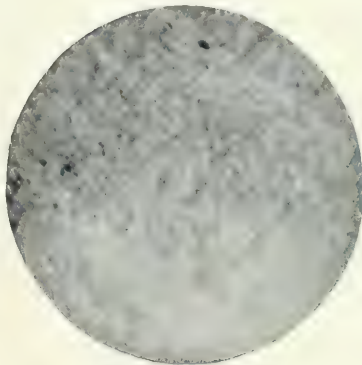
39—Quenched at 2300° Fahr.



40—Quenched at 2400° Fahr.



Series C. No. 30.

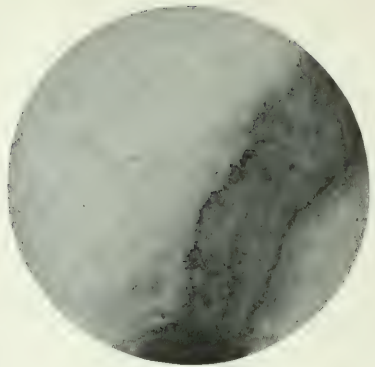


No. 31.

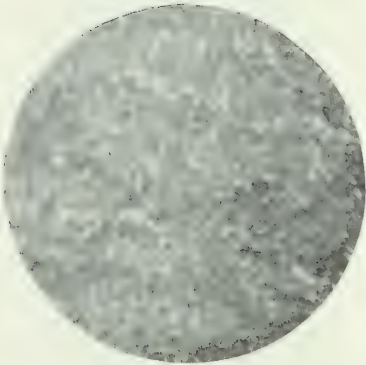




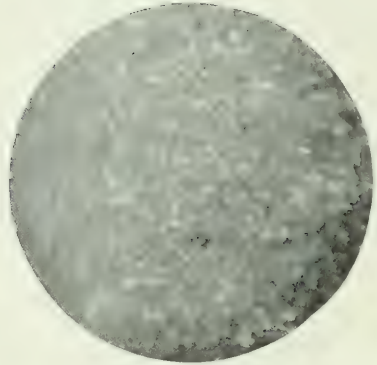
No. 33



No. 33



No. 35



No. 35.



No. 36



No. 37.

Specimen No. 38 shows a distinct difference from the ones just preceding and following, indicating that this steel has a narrow range of temperature in which it can be treated with the best results. This specimen shows the clearest and cleanest structure and is microscopically the best specimen of the group.

In the reproduction of one of the photographs from specimen No. 33 is shown a case referred to in paragraph No. 24. It illustrates the cracking of a specimen which has been heated too rapidly, and quenched before the heat had been allowed to uniformly penetrate to the center of it. However, it does appear remarkable that this specimen did not break under the physical test.

The illustrations from photographs of the fractures show the increase in size of grain as in the preceding series.



No. 38.

*Red Hardness as Affected by the Structure of the Steel.*—The property named *red hardness* in a high-speed tool steel, and which enables it to cut metal when the cutting edge and near portions are heated to a dull red, should, to a certain extent, be related to the structure of the steel according to the above statements.

The heat which is generated by friction between the steel crystals (these being caused to move by vibration) does not destroy the tool as rapidly as the grinding on the crystals by the separated hard constituents, which are present at some temperatures. As the structure of the steel in this case generally consists of crystals of an uneven size, the smaller ones of these are ground to pieces in a comparatively short time, and the cutting edge of the tool is ruined.

Therefore, a uniform size of crystals without separated hard constituents between them in the structure of the tool steel will give a large amount of *red hardness* or high durability, considering the structure of the steel only and apart from the various effects of the chip upon the tool in cutting metals.

To find the element, or combination of elements, in the steel responsible for the highest durability, requires the most elaborate experimenting, in the making of the steel, the heat treatments, and the physical tests, and is beyond the object of the experiments described in this paper. However, it is seen that two slightly different chemical compositions of the steel, subjected to the same heat treatment, show a great difference in durability.

Taking the results of these experiments as a whole, the general shop rule for treating a high-speed tool—"Heat it to a white heat and quench it"—does have its shortcomings, because a variation of 50° F. cannot be determined by the eye.

What are the results of a poorly treated tool? It decreases the shop production for the manufacturer, who allows it inside his establishment.



No. 40

It increases the bill of the customer, who pays for the tool and the work spent on it.

When the works manager comes through the shop and inquires about the tools, the workman naturally testifies the tool steel to be of inferior quality, which, as we have seen, may not be the case, but this tool steel maker has to find a new market for his stock of steel.

In short, it is waste of energy and waste of capital.

#### APPLICATION OF ELECTROSTATIC SEPARATION TO ORE DRESSING.<sup>1</sup>

By F. S. MACGREGOR.

The possibility of utilizing the differences in the electrical conductivity of various minerals by giving a part or all of the particles of ore an electrostatic charge has for several years been recognized as a means of separation, and a large amount of experimenting has been done along this line. The com-

<sup>1</sup> A paper presented at the Eighteenth General Meeting of the American Electrochemical Society, in Chicago, October 13-15, 1910.

mercial application of the art of electrostatic separation has been tried a number of times within the last decade, but until only within about three years has success attended the efforts.

Two factors contributed to this want of success—a lack of the proper means of continuous electrification and a practical machine and system of treatment designed to meet the rigorous requirements of mill operation. Recognizing these conditions, the Huff Electrostatic Separator Company, of Boston, has perfected several types of separators and a means of electrification which have been a commercial success from their first installation, and at present the entire concentrating and separating machinery of two plants consists of Huff separators—one located at Platte-

ville, Wis., and the other at Midvale, Utah. The ore is fed across the first electrode, and it passes by gravity to each succeeding one. The mineral particles receive their charge while passing through a concentrated static field formed by two electrodes—one a grounded rotated shaft, and the other an insulated metal rod. The electrostatic charging of the electrodes is accomplished by a special electrical apparatus (using commercial dynamos and transformers), which, with no more than the usual oiling, gives either a continuous and steady potential of several thousand volts, or an intermittent or pulsating charge of great regularity. The potential, or strength of the field, can be altered at will, according to the conductivities of various ores treated. The figure shows the scheme of separation, the dotted lines



Fig. 1.—Electrostatic separating plant, American Zinc Ore Separating Co., Platteville, Wis.

ville, Wisconsin, owned by the American Zinc, Lead and Smelting Company, and the other at Midvale, Utah, owned by the United States Smelting, Refining and Mining Company. Also a plant is being installed in Nevada.

The type of machine is shown in the accompanying illustration, and consists of a series of separating electrodes placed one above the other. The frame is cast-iron, built in sections, with two electrodes to each section, which facilitates easy shipment and also flexibility in the number of treatments which can be given the ore, and which is dependent on its requirements. A three-section machine (the usual type) is six feet high, six feet six inches long, and eighteen inches wide. A feed hopper on the top distributes

indicating in general the path of the conductors and non-conductors.

The separating plant at Platteville was started in March, 1908, and was the first plant to be equipped with Huff separators. Although originally built as an experimental plant, it has been in practically continuous operation since then, and used to separate, without roasting, the iron pyrite from the zinc blende, which occur together in varying proportions in southwestern Wisconsin. The ores are milled in ordinary jigs and the lead and lime rock removed. Owing to the nearness in specific gravity of the blende and pyrite, they are recovered in the jigs as a middlings, containing from 10 to 45 per cent. zinc, according to the grade of the crude ore, the remaining percentage be-



ing iron and the sulphur in combination. Iron above a few per cent. interferes with the smelting of the blende, and the function of this plant is to remove this pyrite, making the low-grade ores into high-grade smelting ores.

The plant consists of a wooden, frame building, 9 x 12 meters (30 x 40 feet), and three stories high. On the first floor are the bins for collecting the finished products as they are delivered from the separators. The second and third floors are separator floors, and in the tower is located the screening system. A spur railroad track runs on either side of the mill, one for cars of raw ore, allowing them to be unloaded either directly into the mill or into storage bins across the track. The other track, which is below the mill level, permits at the same time the loading of empty cars with finished products.

The course of the ore through the plant is shown

There are four, giving an oversize and four other sizes, called A, B, C and D. In general, the sizes are as follows:

A size.....	6 x 5 mesh (7.00 x 8.00 mm.)
B size.....	10 x 7 mesh (4.00 x 6.00 mm.)
C size.....	24 x 20 mesh (0.16 x 0.20 mm.)
D size.....	50 x 50 mesh (0.08 x 0.08 mm.)

The oversize passes through a short trommel to remove any foreign materials, and is spouted to the first floor to a set of rolls, which crush it and deliver it to the boot of the elevator carrying the original feed.

The location of the screens in a tower permits the different sizes to flow by gravity through iron pipe 5 cm. (2 inches) in diameter to the top machine floor. On this floor are located the rougher machines, where the ore is given a rough split, that is, two products are made, one a product higher in zinc than the original feed, and the other higher in iron. Thus, no matter what the grade of the feed to the mill may



Fig. 2.—Electrostatic separating plant, showing loading trestle, U. S. Smelting Co., Midvale, Utah.

in the flow sheet, and may be described in detail as follows: It is shoveled into a wheelbarrow in the freight car, wheeled to scales and weighed, then dumped into the feed hopper of the drier. The top of this hopper is on a level with the car floors to facilitate easy handling of the ore, and at the bottom of this hopper is an adjustable plunger feeder. The drier is of the cylindrical type, and the shell is 5 meters (16 feet) long and 0.75 meter (30 inches) in diameter, rotating about  $4\frac{1}{2}$  r. p. m. Being set at a slight pitch, the ore travels gradually to the discharge end, where it emerges bone-dry. As the separation depends on the difference in conductivity of the minerals, it is necessary that all moisture be removed. A short drag conveyor carries the dried ore to the foot of a bucket elevator, which raises it to the top of the tower and discharges it into a set of screens.

be (and it varies within wide limits), a fairly uniform mixture is sent to the finishing machines on the floor below.

These finishing machines give the final cleaning to the ore, one set giving a finished iron product and the other a finished zinc product. The middlings from these cleaners return by gravity to the boot of the elevator and mix with the fresh ore, so that no ore leaves the system that is not separated into its proper grades of product.

The finished zinc product and finished iron product fall into separate bins on the first floor. These bins are V-bottomed, and constructed of two thicknesses of wood flooring with heavy building paper between. They are elevated from the floor so that they may conveniently be drawn off into a 730 kg. (1,600 lb.) capacity push car for loading.

The car is then wheeled to a small elevator and dumped into a hopper on the floor level. This feeds the ore into the boot of a small elevator, which discharges either into a freight car by means of a goose-neck spout, or may be allowed to discharge to a second

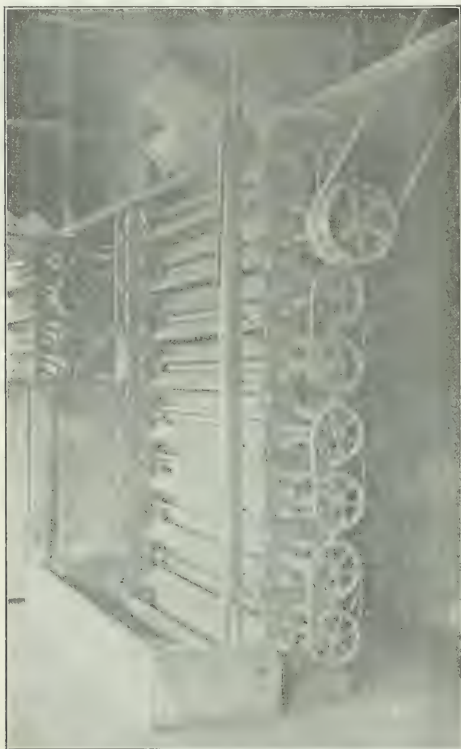


Fig. 3.—Huff electrostatic separator.

elevator in the storage bins. From these bins a car may be loaded whenever convenient.

The plant generates its own power, and the engine and boiler rooms are located in an adjoining building. The fire boxes of the boiler and drier are side by side, enabling the engineer to look after both fires as well as the engine room. Power is supplied by a Corliss engine, connected to the mill by a clutch.

The plant operates continuously three shifts per day. The labor required per twenty-four hours is as follows:

- 3 shift bosses (8 hours each).
- 3 machine helpers (8 hours each).
- 3 drier feeders (8 hours each).
- 2 loaders (10 hours each).
- 2 engineers (13 and 11 hours each).

There is also a superintendent, master mechanic, assayer, one buyer and bookkeeper, although the buyer and, to a large extent, the assayer devote their time to obtaining custom work.

Two products of marketable value are obtained: The iron pyrite, hitherto valueless in these Wisconsin ores, is sold for its sulphur content, and by reason of its free-burning qualities, makes a very desirable product for the acid manufacturer; and a zinc product, which is, of course, sold for spelter. The pyrite is sold by contract, but the blende is sold to the smelters on the open market. With a penalty for excess of iron or lead, one may see it is necessary for such a plant to turn out consistently high-grade products in order to command a satisfactory market price.

The results taken from the "Record of Shipments" for a month show an average zinc product of 55.2 per cent. Zn and 3.4 per cent. Fe, and a pyrite product of 3.7 per cent. Zn and 44.7 per cent. S. The average zinc content of the ore bought and separated into the above products was 24.1 per cent. Zn, and the average iron content was 25.4 per cent. Fe. The minimum zinc content was 6.7 per cent. Zn, and the maximum 41.2 per cent. Zn. The high grade of the separated products shows the flexibility of the process and the ability of the plant to handle any grade of ore from the district.

As a result of the excellent showing of this electrostatic plant, the United States Smelting, Mining and Refining Company decided to put in a plant at their works at Midvale, Utah. The function of an electrostatic plant there is different from that in Platteville, for the ore from the mine of the United States Company, at Bingham, Utah, contains about 9 per cent. of zinc in addition to the gold, silver and lead values.

This ore is shipped to the concentrator at Midvale, where it is crushed and milled by the usual methods of jigs and tables. In this concentration there were formerly two products, one a lead-pyrite product carrying the iron and considerable zinc, and a tailings carrying zinc and some gold and silver values, the object being to keep the zinc as low as possible in the

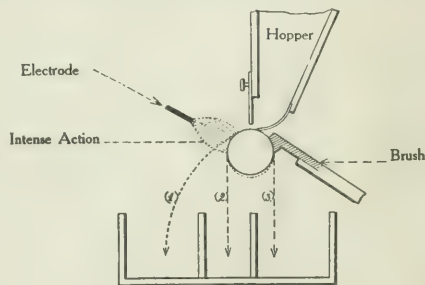


Fig. 4.—Section of electrostatic separator, showing principle of operation.

lead concentrate, and yet at the same time make the maximum recovery of the gold, silver, lead and copper values. The zinc added materially to the

difficulty and cost of smelting the lead concentrates, and, at the same time, was a total loss. In order to recover this zinc, three products were made in the concentrator, a lead-pyrite carrying practically no

separated, and the products drawn from the bins on the first floor into tramcars. These are run out of the mill to the loading trestle and dumped into freight cars. The pyrite product is smelted in the United States smelter near-by, and the zinc product shipped to the Kansas zinc smelters.

The plant is electric-driven by a 20 h. p. motor, the 15 Huff separators requiring about  $1\frac{1}{3}$  h. p. each. The generating apparatus for the electrostatic field is located in a small room on the finishing floor. A 3 h. p. motor is direct coupled to a generator, and the strength of field is controlled from a small switch-board. The plant is operated in conjunction with the concentrator, and the superintendence, assaying and bookkeeping are taken care of by the smelter staff.

The average assays of the feed and products are as follows:

	Oz. per ton.							
	Au.	Ag.	Cu.	Pb.	SiO <sub>2</sub>	Fe.	Zn.	CaO.
Crude ore to concentrator.....	0.08	3.8	0.41	8.4	28.8	14.3	9.0	6.0
Middlings to electrostatic plant.....	0.05	2.8	1.11	3.3	4.6	24.3	21.6	1.9
Finished pyrite.....	0.14	4.8	2.24	6.6	...	26.0	9.0	...
Finished blende.....	0.02	1.5	0.61	2.0	...	3.6	52.9	...

This electrostatic plant not only removes the objectionable zinc from the lead-pyrite concentrate, but makes of it a marketable product, and, instead of being a total loss, it is made to produce a profit. The electrostatic process in these two plants demonstrates two applications in ore dressing, one the custom plant making low-grade ores profitable, and the other as an adjunct to a wet concentrator for the recovery of zinc.

Besides these plants, there is being installed in Nevada a plant working on crude silver ores, wherein the ore goes through no concentrating machinery prior to its electrostatic treatment. The process has been proved applicable to many special problems such as the concentration of copper and lead-silver ores in

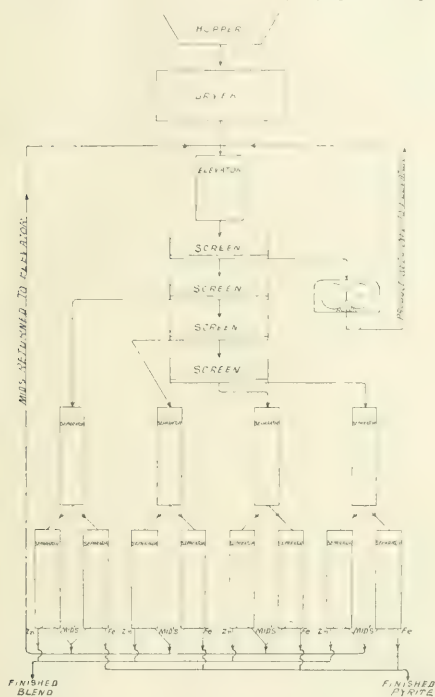


Fig. 5.—Flow-sheet, showing course of ore through the mill.

zinc, tailings free from zinc, and middlings containing about 22 per cent. zinc, the balance pyrite and some copper, lead, gold and silver.

To treat these middlings, an electrostatic plant was built near the concentrator as shown. It is a wooden frame building 12 x 12 meters (40 x 40 feet) and covered with corrugated sheet-iron. In general plan it is the same as the Platteville plant—finished ore bins on the ground floors, and two floors of separators. The method of handling the ore is somewhat different. The middlings are shoveled from the table hutches in the wet concentrator into tramcars, which are pushed by hand to the platform elevator at the electrostatic plant. The cars are raised to the third floor level, and, after weighing, are dumped into a 40-ton hopper. This is built over the drier, and feeds automatically. After drying, the ore is screened as follows, making A size 12 on 24, B size 24 on 50, C size through 50-mesh.

The oversize is small in amount and very low in zinc, so instead of recrushing, it is put directly into the finished pyrite. The three sizes, A, B and C, are

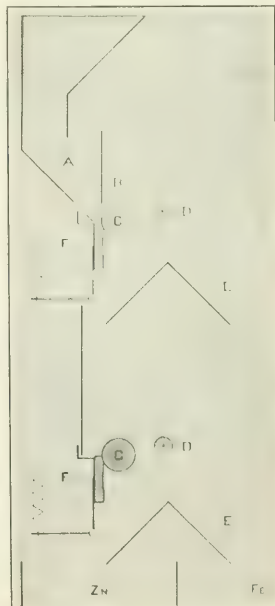


Fig. 6.

- A—Hopper.
- B—Feed gate.
- C—Grounded electrode.
- D—Charged electrode.
- E—Adjustable divider.
- F—Brush.



TABLE OF ELECTROSTATIC SEPARATIONS.

Material.	Product.	Per cent. Cu.	Per cent. Fe.	Per cent. Pb.	Per cent. Zn.	Per cent. SiO <sub>2</sub> .	Oz. Au.	Oz. Ag.
Low-grade chalcopyrite in quartz	Original.....	2.56	17.8	.....	.....	.....	0.01	2.6
	Concentrates.....	5.63	37.0	.....	.....	.....	0.02	5.5
	Tails.....	0.10	2.0	.....	.....	.....	trace	0.4
Pyrite and chalcopyrite in various gangues	Original.....	6.37	25.0	.....	.....	.....	.....	.....
	Concentrates.....	9.33	36.3	.....	.....	.....	.....	.....
	Tails.....	0.14	1.9	.....	.....	.....	.....	.....
Chalcopyrite and bornite in garnet	Original.....	3.60	18.6	.....	.....	32.3	(iron partly in sulphide and partly in garnet)	
	Concentrates.....	19.10	25.7	.....	.....	14.4		
	Tails.....	0.34	17.6	.....	.....	36.7		
Zinc, iron and silver ore.	Original.....	2.61	23.8	13.9	19.4	.....	.....	52.8
	Concentrates.....	3.33	30.7	16.4	6.4	.....	.....	69.0
	Tails.....	0.91	3.4	2.7	51.8	.....	.....	4.6
Zinc, lead, and iron middlings	Original.....	.....	20.2	12.6	23.1	5.2	.....	.....
	Concentrates.....	.....	31.2	21.0	4.0	3.2	.....	.....
	Tails.....	.....	2.4	0.5	53.8	8.5	.....	.....

Material.	Product.	Per cent. Cu.	Per cent. Fe.	Per cent. Pb.	Per cent. Zn.	Per cent. S.	Per cent. SiO <sub>2</sub> .
New Mexico concentrates.	Original.....	2.11	16.2	.....	29.9	.....	12.9
	Concentrates.....	5.65	37.2	.....	4.9	.....	6.6
	Tails.....	0.13	4.2	.....	44.9	.....	15.9
Zinc from above tailings	Original.....	.....	.....	.....	.....	.....	.....
	Concentrates.....	.....	.....	.....	57.1	.....	.....
	Tails.....	.....	.....	.....	1.3	.....	.....
Native copper in sandstone..	Original.....	2.68	.....	.....	.....	.....	.....
	Concentrates.....	38.70	.....	.....	.....	.....	.....
	Tails.....	0.27	.....	.....	.....	.....	.....
Pyrite concentration for sulphur	Original.....	.....	.....	.....	.....	30.1	.....
	Concentrates.....	.....	.....	.....	.....	44.8	.....
	Tails.....	.....	.....	.....	.....	3.0	.....
Middlings from Joplin, Mo.	Original.....	.....	10.8	2.5	49.5	.....	.....
	Concentrates.....	.....	37.4	9.9	2.9	.....	.....
	Tails.....	.....	1.6	trace	62.3	.....	.....

heavy gangues such as garnet, barite, epidote, etc. The accompanying table will give some idea of what can be expected with several of these problems.

The perfection of the art of electrostatic separation marks an important step in the dressing of complex or difficultly milled ores.

## EFFICIENCY IN THE ELECTROLYTIC PRODUCTION OF METALLIC CALCIUM.<sup>1</sup>

By FRANCIS C. FRARY, HENRY R. BICKNELL AND CARL A. TRONSON.  
Received October 12, 1910.

Most of those who have worked on the electrolytic production of calcium have been content to describe their methods and apparatus, with perhaps an analysis of a selected lump of their product, but say nothing of the current efficiency obtained. Muthmann,<sup>2</sup> in the discussion of a paper by Rathenau, states that by using an electrolyte consisting of two parts of calcium chloride to one part of the fluoride, and raising the iron cathode as the metal accumulated, he obtained a "good" yield. Goodwin,<sup>3</sup> electrolyzing pure calcium chloride in a similar way, obtained a

current efficiency of 21.5 per cent. to 41.9 per cent. Woehler,<sup>1</sup> using an electrolyte containing 100 parts of the chloride to 17 parts of the fluoride, claims an efficiency of over 80 per cent., but states that the electrolyte deteriorated in time, probably owing to the formation of the hydrated oxychloride, and that hydrogen (!) is then liberated at the cathode, and the yield decreases. He used a current of 40 amperes at 33 to 38 volts, but does not say how often or for how long a time this efficiency could be obtained. Tucker and Whitney<sup>2</sup> improved the apparatus of Goodwin, and claim an efficiency of 60 per cent., using the pure chloride as electrolyte, but give no data to support the claim. As far as we are able to ascertain, no one else has published any results on the efficiency of the various processes which have been proposed.

During previous work in this laboratory,<sup>3</sup> efficiencies as high as 46 per cent. were obtained, but, unfortunately, the only runs in which the necessary data were taken were made under unfavorable conditions. As it was certain that better results could be obtained and had been obtained in some of the runs for which no data were at hand, these were not published at the time, and the work was continued by the present authors.

<sup>1</sup> A paper presented at the Eighteenth General Meeting of the American Electrochemical Society, in Chicago, October 13-15, 1910. The work described in this paper is a continuation of that published by Frary and Badger (*Trans. Am. Electrochem. Soc.*, **16**, 185) where a summary and discussion of previous work on the electrolytic production of calcium will be found.

<sup>2</sup> *Z. Elektrochem.*, **10**, 508 (1904).

<sup>3</sup> *J. Am. Chem. Soc.*, **27**, 1403 (1905).

<sup>1</sup> *Z. Elektrochem.*, **11**, 612 (1905).

<sup>2</sup> *J. Am. Chem. Soc.*, **28**, 84 (1906).

<sup>3</sup> Frary and Badger, *Loc. cit.*

The apparatus used was the same as that described by Frary and Badger,<sup>1</sup> and consisted essentially of a large crucible of Acheson graphite having a water-cooled bottom and serving as anode, and a water-cooled iron cathode a little over an inch in diameter. The crucible was enclosed in a protective layer of refractory material, and special pains were taken with the contact between it and the positive cable. The cathode could be raised or lowered at will by means of a screw mechanism.

From preliminary experiments, it was decided that the occasional feeding of the fresh electrolyte and irregular raising of the cathode were two important causes of low efficiency. Intermittent addition of electrolyte caused irregularities in the height of the melt and its temperature, especially the latter. Too great cooling of the electrolyte caused the deposition of the metal in a spongy form, in which state it was readily lost. Spongy portions were also formed when the stick of metal extended too far below the surface of the melt, the current density<sup>2</sup> being insufficient to melt the metal at the point of contact with the electrolyte, and thus produce a solid stick. This spongy metal was very likely to be dislodged and swept away by the vigorous convection currents which were always present; it also gave trouble by growing toward one side or other of the crucible, causing an increase of current at that point, with consequent increased growth of metal and a higher temperature, until finally the calcium on the edges would melt, and, being connected with the main stick only by thin pieces of metal, would be easily swept away by the electrolyte. When the end of the stick of metal was kept just below the surface of the electrolyte, the spongy metal at first formed melted almost at once, and its surface tension drew it into a compact globule which was almost immediately frozen by the cooling effect of the rest of the stick and the water-cooled cathode. Thus a solid stick was easily obtained. To get the best results, it was found necessary for one person to devote all his attention to the raising of the cathode and the addition of the electrolyte, making both operations practically continuous.

The chloride used was some of Merck's C. P. granulated, which had previously been used in desiccators. It was dried in an iron crucible over a four-post Bunsen burner, and preserved in a stoppered bottle.

In starting up a run, the cold fused chloride remaining in the crucible from a previous run was heated until dry by directing the flame of a blast lamp upon it. Then a small portion of it was fused by drawing an arc from the side of the crucible with the aid of a graphite rod. A small current was used until contact was made with the cathode, when more cur-

rent was put on and the graphite rod removed. As soon as good contact was assured, the direct current was shut off and an alternating e. m. f. of about 30 volts applied. The current usually rose rapidly to about 200 amperes, being regulated by raising or lowering the cathode, and the upper part of the crucible was soon filled with the molten chloride. A sufficient supply of electrolyte was added at the time to fill up the crucible, and when all was ready the alternating current was thrown off and the direct current thrown on. Readings of the time, voltage and amperage were taken at once. The voltmeter and ammeter were read every five minutes during the run, and the average of these readings considered to be the average voltage and amperage for the run. The current varied very little during each run, as it was taken from the 110-volt lighting circuit through a constant resistance. There was no trouble with the so-called "anode effect," except when the electrolysis was started before a sufficient amount of the electrolyte had been melted down by the alternating current.<sup>1</sup>

The formation of the metal under the cathode was watched very carefully, great care being necessary to get a good start. We aimed to withdraw the cathode and metal as rapidly as it was possible to do so without striking an arc. It will be noticed in the table of results that practice in doing this increased the yield obtained. When the electrolysis is going on properly, and the stick of metal is at the right depth, the electrolyte seems to flow rather rapidly across the surface in a fixed direction, and is hottest at the cathode. The operator must be guided by the appearance of the electrolyte at the cathode. There should be a rosette-like spot with radial markings here; if the stick of metal is pulled out too fast, this spot becomes almost white hot, and if the metal is not at once lowered, an arc forms, and part of the metal is melted off and lost. If the stick is not raised fast enough, the spot becomes less noticeable, and spongy metal deposits below the surface, causing losses. When the electrolysis was well under way, new electrolyte was added in small portions, taking care to make these additions as continuous as possible, and in such a spot that the convection currents carried the cold chloride away from the metal. The following table shows the efficiency obtained.

The sticks of metal were cleaned by hammering off the crust on the outside, and then placing them in absolute alcohol for 24 hours to remove the rest of the chloride. When taken out of the alcohol, the sticks were always clean, though covered by a thin coat of oxide. They were dried by burning off the

<sup>1</sup> A sample of the electrolyte was taken at such a time, when the "anode effect" had been more than usually troublesome, and the per cent. of silica present determined. Only 0.036 per cent. was found, confirming the results obtained in the previous paper, and indicating that current density rather than impurities should be blamed for this "effect."

<sup>2</sup> Loc. cit.

<sup>2</sup> In most cases a rod of about 1 cm. diameter was obtained, so the cathode area was about 1 to 1.5 sq. cm.

alcohol, and weighed. The current was, of course, not absolutely constant, so there is a possible error of one or two per cent. in the efficiency as calculated, but the results are sufficiently accurate for practical purposes.

TABLE I.

Run No.	Time. Min.	Amperes.	Volts.	Weight. Grams.	Efficiency. Per cent.
1	60	74.45	18.3	30.8	55.3
2	60	73.9	21.4	25.0	45.2
3	60	74.2	21.0	43.5	78.4
4	38	73.2	26.0	27.0	77.8
5	32	73.1	24.4	26.5	90.7
6	30	71.5	25.5	24.0	89.8
7	27	70.4	33.0	21.5	90.5
8	30	69.66	28.0	26.0	100.0
9	34	52.54	34.0	21.6	97.0
10	36	68.75	31.0	31.0	100.5

Since Ruff and Plato,<sup>1</sup> Muthmann,<sup>2</sup> and Woehler<sup>3</sup> have recommended the use of a mixture of the chloride and fluoride as the electrolyte, we decided to try it and see if it offered any advantages. The fluor-spar partially purified by treatment with concentrated hydrochloric acid to remove iron. It was mixed with the chloride in the proportion of 16.5 parts to roo, as recommended by Ruff and Plato. A new crucible was made for use with this electrolyte, having the same size as the other, but a different arrangement of the water-cooling. The bottom of the crucible was turned out on the lathe so as to fit loosely over the hollow brass cooling cylinder of the Borchers's<sup>4</sup> furnace for the electrolysis of fused salts. The crucible was then turned upside down, this space filled with a strong copper sulphate solution, and copper deposited until the cylinder would not enter the space. The copper was now turned out on the lathe to fit the cylinder, and the whole of the outside of the crucible and cylinder protected from the air by a coat of Portland cement and carborundum fire-sand, held in place, as before, by a tin form. The contact, being made through the water-cooling cylinder, was kept cool and did not burn away, as the other crucible did in the course of time. A more complete protection of the outside of the crucible was also possible.

With this crucible and the above-mentioned electrolyte a new series of runs was made. Considerable trouble was found in making smooth, solid sticks of metal with the electrolyte. The particular advantage of this mixture is supposed to be its low melting point (660°). This appears to us to be a disadvantage, as the bath must be worked at a temperature of nearly 750° in order to get a solid stick of metal, and the bath is so fluid at the working temperature that convection currents are more violent and more likely to sweep away the metal from the end of the stick, forming an arc. We had a great deal of trouble

from this cause. Reduction of the current did not bring the desired result, as the efficiency decreased markedly (Run No. 6, Table II). The following results were obtained:

TABLE II.

Run No.	Time. Min.	Amperes.	Volts.	Weight. Grams.	Efficiency. Per cent.
1	30.0	42.0	....	15.0	95.5
2	32.5	41.5	31.0	15.0	89.2
3	42.0	53.9	37.0	27.0	95.7
4	35.0	45.6	31.3	12.8	64.4
5	9.0	54.9	26.0	8.0	81.2
6	41.0	31.9	30.0	5.0	30.6
7	45.0	52.1	29.5	18.0	61.6
8	45.0	53.5	30.7	26.0	86.6
9	46.0	69.3	31.4	29.4	74.0
10	40.0	52.7	34.0	22.6	86.0
11	35.0	53.5	30.8	20.0	85.5

During the runs with this electrolyte only the chloride was added, it being assumed that the fluoride would not be decomposed. However, at the close of these experiments, a sample from the top of the melt showed only 2.21 per cent. of insoluble matter, so, evidently, much of the fluoride had been lost. This loss was probably largely mechanical and due to the violent spattering of the electrolyte; it was noticed that a great deal more of the fine dust from the electrolyte collected on the crucible and its surroundings with this than with the simple chloride electrolyte.

We also took samples from the electrolyte in the lower part of the crucible, which had been kept frozen during the electrolysis by the cooling coil, and so, presumably, retained its original composition, and attempted to isolate the fluochloride of calcium described by Poulenc<sup>1</sup> and Defacqs,<sup>2</sup> but found none of it.

From our experience with both electrolytes we believe that the plain chloride is a little more satisfactory than the mixture of the chloride and fluoride in point of efficiency, and decidedly easier to manipulate. We have shown that satisfactorily high efficiencies can be obtained with it, and that efficiency is more largely a matter of careful regulation of conditions than anything else.

UNIVERSITY OF MINNESOTA,  
September 9, 1910.

### SOME IMPERFECT PAVING BRICKS.

By JAMES C. LAWRENCE AND CHARLES J. BONER.  
Received October 1, 1910.

It was noticed by the authors that a paving-brick manufacturing company near this city was making quite a large number of imperfect bricks, along with their good ones. These bricks were imperfect in that they were distorted and contained a dark gray scoriaceous core (see figure). These bricks were of course worthless for paving or construction work, for even if they were not swollen out of shape, the scoriaceous core weakens them to a considerable extent, as shown

<sup>1</sup> Ber., 35, 3612 (1902); 36, 491 (1903); D. R. P. 153,731 (Chem. Centr., 1904, II, 802).

<sup>2</sup> Z. Elektrochem., 10, 508 (1904).

<sup>3</sup> Ibid., 11, 612 (1905).

<sup>4</sup> Borchers, "Die Elektrische Oefen," 1907 ed., pp. 35 and 36.

<sup>1</sup> Ann. chim. phys., [7] 2, 5 (1894).

<sup>2</sup> Ibid., [8] 1, 337 (1904); Compt. rend., 137, 1251 (1903); J. Chem. Soc., 86, ii, 123 (1904).



by some standard tests. The perfect bricks stood a cross-breaking test of from 6,000 to 9,000 pounds, while the swollen ones showed only about 2,500 pounds on the Olsen machine. At the time of making our preliminary tests we also found that the company was discarding a layer of shale at the pit, about ten feet thick and one hundred feet along the face, simply because they *thought* it wouldn't make good bricks, it being a little darker in color than the other strata of shales. We decided to look into that shale also, to see what bearing it could have on the bricks made if used.

Samples of all the shales used in making the bricks were obtained from the pit, beginning at the top, and calling it Sample No. 1, and obtaining three other samples each ten feet lower down the face of the pit than the immediately preceding sample, taking three samples in each stratum.

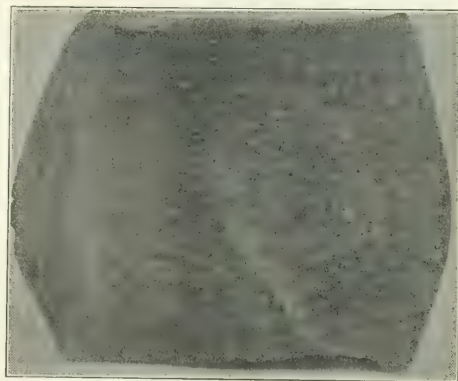
The imperfect and good bricks were selected at random from a pile in the yard. All the samples were ground to pass an 80-mesh sieve, then kept in glass-stoppered bottles until used. Duplicate analyses of each shale and brick were made, the results of which are shown in the table, expressed as the mean values of the analyses:

Imperfect bricks.

	Shale 1.	Shale 2.	Shale 3.	Shale 4.	Shell.	Core.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
SiO <sub>2</sub> .....	63.33	66.67	64.85	55.79	58.99	60.01
Fe <sub>2</sub> O <sub>3</sub> .....	6.29	6.77	1.16	1.22	19.06	5.64
FeO.....	1.46	5.06	7.36	9.56	1.23	12.27
Al <sub>2</sub> O <sub>3</sub> .....	14.51	9.81	14.66	17.65	12.87	12.68
CaO.....	0.71	1.15	1.56	0.40	1.33	1.25
MgO.....	1.46	0.16	0.17	1.96	2.03	2.17
Moisture <sup>1</sup> .....	3.04	0.95	0.94	1.42	trace	0.05
Loss <sup>2</sup> .....	4.55	4.52	4.90	6.64	none	0.39
K <sub>2</sub> O.....	1.12	1.11	0.82	2.95	1.95	1.79
Na <sub>2</sub> O.....	2.75	3.23	4.27	1.54	2.86	2.62
H <sub>2</sub> O <sup>3</sup> .....	...	...	...	...	none	0.36
S <sup>4</sup> .....	0.13	trace	trace	1.71	0.30	1.46

Proceeding with the first question: that of the fitness of the shale No. 1 for making bricks, we see by comparing with the others in the table that it shows practically the same values, merely being a little higher in ferric iron. The state of the iron in this sample is due to its being more exposed to the weather, since it was taken from near the surface. It will be noted that the ferrous iron content increased as we obtained the samples farther down the face of the pit, and since the bricks were being made of the dark shale at the bottom of the pit, their ferrous iron content was high until oxidized in the burning. In as far as the ultimate chemical analysis of a shale can show its adaptability for brick-making, this shale (No. 1) is as good as any of the others, and perhaps better than No. 4, for the manufacture of paving-brick,

for No. 4 has too high a sulphur content. This sulphur, as pyrites, in a shale is very objectionable, for it forms a ferrous silicate that is very hard to oxi-



dize in the burning of the brick,<sup>1</sup> and will remain as a very brittle black slag, making a poor brick for paving purposes.

In the distorted bricks referred to at the beginning of the article, the question arises as to what causes the distortion and the black core. From the table it can be seen that there are only three main differences in composition of the outer shell and the inner core of the bad bricks. These are in ferrous iron, in sulphur, and in combined water content. The question then arises as to which of these causes the swelling and the difference in color and texture. Going back to the analyses we see that all the shales are rather high in the so-called "fluxing oxides" (those of Mg, Ca, Fe, Na and K). Therefore, if heated rapidly to a high temperature fusion begins, and naturally the outside of the brick fuses first. We have shown that the inner core of the brick contains some combined water, while the outer shell does not. Hence, the vitrification on the outside having taken place before the interior of the brick was completely dry, the water was set free as steam, and, having no outlet through the vitrified shell, exerted a great pressure within, thus causing the distortion and the scoriaceous appearance of the inner core. This fact, the incomplete burning of the inner part of the brick, is further proved by the fact that the sulphur, which is present as pyrite, is almost completely burned off in the outside shell, while the amount in the inside is practically the same as shown in the shale itself. The dark color of the interior is attributed to the ferrous iron, which the analyses show to be much higher in the interior of the brick.

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<sup>1</sup> Purdie, *Bull. 9*, Ill. Geol. Survey.

<sup>1</sup> Water at 100° C.

<sup>2</sup> Includes "combined water."

<sup>3</sup> Combined water as found with special apparatus.

<sup>4</sup> Present as pyrites.

THE NORMAL WEIGHT OF DEXTROSE.<sup>1</sup>

By C. A. BROWNE.

Received August 1, 1910.

There is perhaps no single constant given in the literature upon sugar analysis which shows such a variation in value as that given for the normal weight of dextrose. The range extends from 32.5 to nearly 33 grams. Landolt<sup>2</sup> gives as the normal weight of dextrose for true cc. 32.65 grams and for Mohr cc. 32.73 grams; Sidersky,<sup>3</sup> in his latest work, gives the figures 32.82 grams for true cc. and 32.765 for Mohr cc.; Tucker<sup>4</sup> and König<sup>5</sup> each give the value 32.68 grams, and this figure is the most common perhaps of any value given in the literature.

The reason for the considerable variation given to this constant is due largely to the fact that each authority has taken a different specific rotation of dextrose as a basis of calculation. There is no other sugar which shows such a difference in specific rotation for variations in concentration as dextrose; the values for specific rotation of dextrose, according to the formula of Tollens,  $[\alpha]_D^{20} = 52.50 + 0.018796\beta + 0.0005168\beta^2$ , range from 52.52 for a 1 per cent. solution to 54.73 for a 50 per cent. solution, which is about the limit of saturation at 20° C.

Landolt<sup>1</sup> gives as the normal weight of dextrose for a 5 per cent. solution 32.91 grams, for a 15 per cent. solution 32.75 grams, and for a 25 per cent. solution 32.50 grams, in which connection he states that in weighing out the dextrose-containing material for polarization, the chemist must select his normal weight according to the amount of dextrose present. This of course involves a preliminary assay of the material under examination, which means practically doubling the work of analysis.

In the case of dextrose, as of all sugars, the author believes that one fixed value should be given to the normal weight, the value to be selected (as in the case of sucrose) being that weight of c. p. sugar which dissolved to 100 true cc. and polarized at 20° C. in a 200 mm. tube will give a constant reading of exactly 100 upon the saccharimeter. If in the use of such a normal weight with impure products readings of less than 100 are obtained, the latter are corrected by a table giving the true percentage equivalent of each division of the saccharimeter scale. The principle is the same as that employed in the well-known table of Schmitz for sucrose.

The author has converted the formula of Tollens for the specific rotation of dextrose from a percentage to a concentration basis, the latter form being more easily applied in the calculation of normal weights.

<sup>1</sup> Paper read before the San Francisco meeting of the Amer. Chem. Soc., July, 1910.

<sup>2</sup> Landolt, "Das Optische Drehungsvermögen" (1898), p. 448.

<sup>3</sup> Sidersky, "Polarization et Saccharimétrie" (1908), p. 100.

<sup>4</sup> Manual of Sugar Analysis (1905), p. 292.

<sup>5</sup> König, "Untersuchung landwirtsch. u. gewerb. wichtig. Stoffe," p. 216.

The formula is thus recalculated as  $[\alpha]_D^{20} = 52.50 + 0.0227c + 0.00022c^2$ . According to this formula the specific rotation of a dextrose solution containing 32.5 grams to 100 cc. (the preliminary value taken for the normal weight) is 53.47. Calling the specific rotation of sucrose 66.5 and its normal weight, as under the present metric cc. standard, 26.00 grams, we obtain by means of the proportion 53.47:66.5::26:x, a value of 32.336 grams as the amount of c. p. dextrose necessary to dissolve to 100 true cc. in order to obtain a constant reading of 100 upon a saccharimeter standardized according to the requirements of the modern Ventzke scale.

The value just calculated is not absolutely correct, however, since it is based upon the assumption that the equivalent of 1° Ventzke upon the circular scale is the same for dextrose as for sucrose. That there is a slight difference in the rotation dispersion of these two sugars as compared with quartz has long been recognized. According to Landolt, the value of 1° Ventzke in circular degrees for dextrose is 0.3448. Brown, Morris and Miller give for a 10 per cent. solution of dextrose the value 0.3442 and for a 5 per cent. solution the value 0.3454, the mean figure being 0.3448, the same as that of Landolt. The value of the 100° point of the Ventzke scale for dextrose may be taken, therefore, as 34.48 circular degrees. The specific rotation of a dextrose solution of 32.34 grams concentration (the value for the normal weight just calculated), according to the preceding formula, is 53.46. Substituting these values in the general concentration formula for specific rotation  $[\alpha]_D^{20} = \frac{\alpha \cdot 100}{l \cdot c}$ , in which  $\alpha$  is the reading in circular degrees,  $l$  the dcm. length of the observation tube, and  $c$  the grams of sugar dissolved to 100 cc., we obtain for a 2 dcm. observation tube the value  $c = \frac{34.48 \times 100}{2 \times 53.46} =$

32.248 grams, or rounding off to the even hundredths of a gram, which can be done without a sensible error, 32.25 as the correct normal weight for dextrose.

The extent of the corrections necessary to be applied to the scale reading of a saccharimeter, when using the above normal weight, is shown by the following table, which gives the scale division, the cor-

Scale division.	Concentration.		Actual dextrose value of scale division.	Correction to be added.
	Grams dextrose 100 true cc. 20° C.	Specific rotation dextrose $[\alpha]_D^{20}$ .		
100	32.250	53.46	100.00	0.00
90	29.025	53.34	90.20	0.20
80	25.800	53.23	80.35	0.35
70	22.575	53.12	70.45	0.45
60	19.350	53.02	60.50	0.50
50	16.125	52.92	50.51	0.51
40	12.900	52.83	40.48	0.48
30	9.675	52.74	30.41	0.41
20	6.450	52.66	20.30	0.30
10	3.225	52.58	10.17	0.17
1	0.323	52.51	1.02	0.02

responding percentage value of the normal weight, the specific rotation of dextrose corresponding to this weight of sugar in 100 true cc. and the actual dextrose value of the scale division.

The correction necessary to be added to any reading (*s*) of the saccharimeter scale, as formulated from the above table, is equal very closely to  $+0.02s - 0.002s^2$ . The percentage of dextrose (*D*) corresponding to any scale reading(*s*) of the saccharimeter is therefore expressed by the formula

$$D = s + 0.02s - 0.0002s^2$$

The advantages of using a fixed value for the normal weight of dextrose as defined are very evident. The percentage of dextrose is found at one operation without the necessity of making a preliminary assay of the material in order to determine the exact quantity necessary to be weighed out. The method is also much more accurate than any of the processes using the variable normal weights prescribed in sugar literature.

The method described for dextrose is one which can be applied to all other sugars. By defining the normal weight for each of the sugars in the manner outlined in this paper, giving it a fixed value as in the case of sucrose, much of the confusion and inaccuracy attending the use of saccharimetric methods in sugar analysis can be avoided.

## MACHINE FOR MILLING SAMPLES OF WHEAT.

By GEO. A. OLSON.

Received October 1, 1910.

A milling outfit which will mill small samples of wheat (50 to 500 grams) as efficiently as the \$550.00 Allis-Chalmers experimental mill can be installed for a sum not exceeding \$10.00. With this outfit it is possible to test the milling qualities of flour, determine the various constituents contained therein, and determine the value of a wheat from a nutritive standpoint as well as the baking qualities.

This inexpensive outfit has been used by the writer in his research work and as a result has proven useful in a number of instances, among which may be mentioned, first, the modifying and remilling of flour; second, the germinating of wheat and its effect on the quality of the flour therefrom; third, determining the milling qualities of Washington wheats and new hybrids; fourth, determining the amount of flour contained in oats, barley, corn, etc.; fifth, the mixing of wheats to determine which combination of wheat makes the best blend for flour; sixth, assisting the State Grain Inspection Department in several instances; and seventh, determining the milling qualities of hybrid wheats from centgener plots. The possibilities for extending the use of this outfit in commercial, as well as experiment station, laboratories, flour mills, grain inspection departments,

commission houses, and among the farmers seem promising from the many ways that it may be used satisfactorily.

In addition to the usefulness of this outfit in work similar to that done by the writer, it may also prove valuable in feeding-stuff work, *e. g.*, for the detection of adulterations in ground feed, which are claimed to be made up of whole grains, when, as a matter of fact, oat hulls, corn cobs, etc., have been admixed. Such adulterations can readily be detected by making a milling determination. In cases of this kind flour determinations will tell more in regard to the nature of the feed than crude fiber determinations. By changing the bolting-cloths for sieves of any desired size, mechanical analysis of soil, the reduction of coal and ore can readily be accomplished.

In the following paragraphs a description of the mill, bolting machine, and the methods of operating the same, are given, together with results showing the efficiency of this inexpensive milling outfit.

*Mill.*—It is needless to state that the success of milling small samples of wheat depends as much upon the efficiency of the mill as it does upon the bolting machine. With the coöperation of the manufacturer of the mill used in this work, the writer finally succeeded in getting one of their standard mills modified in such a way that it will reduce wheat into flour as satisfactorily as if the wheat had passed between rollers. The mill has been thoroughly tested on both hard and soft wheats. It has been found, however, that it takes a little longer to reduce hard wheats than soft ones. In addition it requires some judgment to mill the same and different varieties of wheat. The mill (Laboratory Special) is manufactured by the Gray Iron Casting Co., Springfield, Ohio.

*Bolting Machine.*—The accompanying drawing shows the construction of the bolting machine used by us. The gearing from an old-style Babcock tester was used, leaving one of the arms on the horizontal wheel long enough so as to allow a three-inch reciprocal motion. Other forms of shaking devices will answer the same purpose. A modified soap box with a platform built about one-third the distance from the bottom to hold a removable drawer, beveled flanged pieces inside the box to permit the flour to drop toward the center of the drawer, and two strips of wood to hold the grooved sliding board (having an opening large enough to hold the bolting frames), which is connected by means of a shaft to the arm on the horizontal wheel, completes the machine. A tin box would be preferable to a wooden box owing to the fact that the smooth surface would tend to remove the danger of loss of flour in sifting and make it easier to collect same.

*Bolting Frames.*—The bolting frames were made out of crayon boxes with the bottoms sawed off. Besides a 20-mesh wire gauze, a No. 30 GG, No. 50

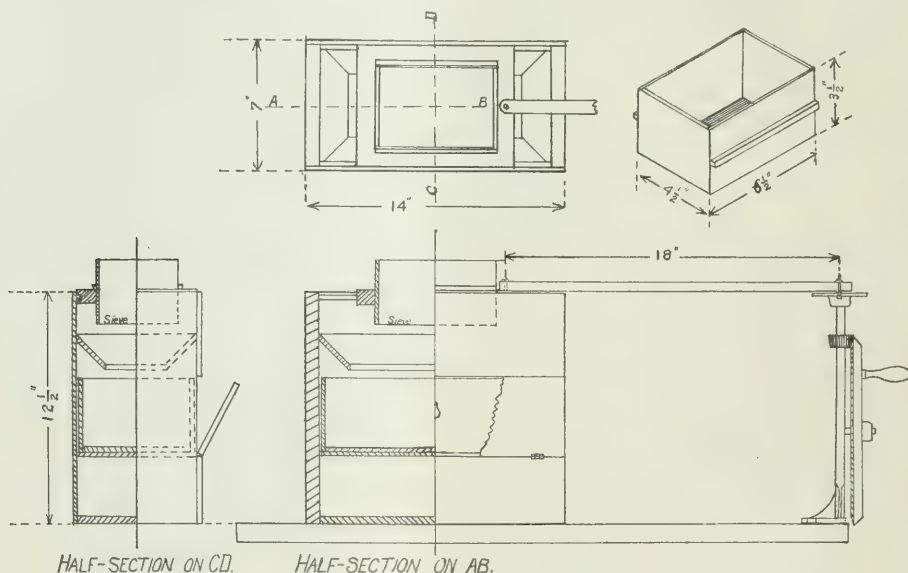


GG, No. 70 GG, and No. 10 XX bolting-cloths were either tacked or glued to the boxes. The frames were reinforced on the sides with two strips of wood so as to prevent them from falling through.

*Milling Process, First Method.*—One hundred grams of cleaned wheat are tempered with approximately a thimbleful of water and allowed to stand for about thirty minutes or so, depending upon the variety of wheat to be milled. When the outer coating (epidermis) feels soft to the touch the sample is ready for grinding. The first grinding should be done with the mill loosely set. The larger particles of bran are then separated from the smaller ones by bolting through the 20-mesh sieve. This process is repeated three times, which will usually be sufficient. The

paper and work as much of unbolted material as will first pass through the 70 GG and finally the 10 XX bolting-cloths, using a coin or iron washer to aid in removing the last traces of flour. The residue remaining on the 10 XX bolting-cloth and including everything to 30 GG is weighed as shorts. The flour is then gathered and weighed and the amount of loss or gain calculated from the difference between the sum total of bran, shorts and flour from one hundred. By rebolting the flour through the 70 GG sieve a couple of times, the sample mixes uniformly and is then ready for carrying out the gluten and baking tests.

*Milling Process, Second Method.*—If the grain of the flour is considered of minor importance, the mill-



BOLTING MACHINE

unbolted material is then ground again with the mill set tighter together and bolted through the 30 GG bolting-cloth, which leaves the germ, fragments of bran and some particles of flour on the bolting-cloth. It will be necessary to grind the unbolted material left on the 30 GG sieve several times in order to reduce the germ and flour particles. The material not passing through the 30 GG and 20-mesh sieves is weighed as bran. Next gather the siftings in the drawer and bolt through the 50 GG bolting-cloth. The unbolted material left on this sieve is then ground again with the mill set tight and the operation of grinding and bolting through the 50 GG sieve continued from two to three times, depending upon the variety of wheat used. Collect the flour on a smooth

ing operation can be simplified by bolting first through 30 GG bolting-cloth to remove bran and then follow by using 10 XX bolting-cloth exclusively. This process consists of tempering the wheat as previously described and alternating the milling and bolting operations. This method of procedure is in every respect as good as the former to determine the yield and quality of the gluten, blending, grading, and determining the composition of the wheat and its products. It should prove as valuable for determining the amount of flour in barley, corn, oats, and supposedly whole grains. In addition, this process saves time and where small quantities of grain are milled more samples can be tested, and as a result more work will be accomplished than is possible for

accurate results with a larger type of mill and bolting machine. The writer, single-handed, has succeeded in milling twice the number that is possible with the Allis-Chalmers outfit with two men. The time required in either case, however, will depend upon the nature of the wheat (hard or soft) and to a large extent upon the condition of maturity of the grain to be tested.

*Suggestions.*—A few words of advice in regard to operating the mill may be of some value to others who may contemplate using this small outfit. Grain should never be crowded nor forced through the mill, rather feed slowly and grind oftener. Set the mill loosely at first and after the bran has been removed the mill should be tightened up to reduce the more flinty part of the wheat. If the wheat is too moist after tempering there is a tendency for the wheat to pack the mill; this is especially noticeable when the wheat is fed in too large quantities. On the other hand, if the wheat is moist and fed a few kernels at a time no packing has been observed to take place. In addition there is a tendency for the mill to heat when grinding and care should be exercised to avoid this as it may alter the quality of the flour.

*Efficiency of Outfit.*—Using samples of the same wheat which the cerealist used in his milling operations on the Allis-Chalmers experimental mill showed that accurate work could be done with the outfit herein described. Since no data were taken by the cerealist in regard to the loss or gain in the milling, the writer had to limit his comparisons to the amount of bran and shorts obtained by the two methods. The largest variation observed was in case of a blue-stem wheat where the writer obtained 2.6 per cent. less bran and shorts than did the cerealist. In the other fourteen cases the results were within a narrow range of each other.

*Other Milling Tests.*—A total of 119 samples of wheat representing different varieties grown in the State of Washington have been milled and bolted and the results for average, maximum, and minimum have been summarized in the following table:

RESULTS OF MILLING TESTS.

	Per cent. bran and shorts.	Per cent. flour.	Per cent. loss. <sup>1</sup>	Per cent. gain. <sup>2</sup>
Average.....	27.37	72.77	1.21	1.01
Maximum.....	38.80	82.00	5.10	3.30
Minimum.....	15.95	60.55	0.03	0.05

The results summarized in the above table show that some wheats when milled lose in weight, while others gain. The gains may be attributed to water absorption, whereas the losses may be due to either unavoidable loss or to the lowering of the moisture content, or both. Out of a total of 119 samples milled, 64 had an average gain of 1.01 per cent., and in one case a gain of 3.30 per cent. Fifty-seven

out of the 64 samples milled did not exceed 1.50 per cent. over the theoretical amount. Fifty-five samples milled had losses, one of which (a New Mexico hard wheat) resulted in a loss of 5.10 per cent. Forty-five out of the 55 did not exceed 1.50 per cent. loss.

The wide variations in the yield of bran and shorts and flour, as is evidenced from the maximum and minimum figures, show the importance of milling samples of wheat in order to determine the relative value of different wheats which are sold.

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## THE REACTION OF LIME AND GYPSUM ON SOME OREGON SOILS.

By C. E. BRADLEY.

Received July 11, 1910.

It is a well-known fact that the soils of Western Oregon respond very readily to even small applications of gypsum. Many instances are recorded where the yield of a clover or vetch crop has been practically doubled by a treatment with plaster at the rate of fifty or sixty pounds to the acre, and this fertilizer has also been used with success by a number of market gardeners on general truck crops.

The reactions which take place in the soil when gypsum is applied have been studied by many investigators. Boussingault compared the analyses of clover on which gypsum had been used with the same plant grown on untreated plats and noted that the plastered clover contained more potash. Storer<sup>1</sup> referring to this action states:

"It is found that the lime of the gypsum is fixed in the soil while a corresponding quantity of sulfate of potash goes into solution. Thus it happens that gypsum not only sets potash free for the use of the crop but it causes potash to be transferred from the upper to the lower layers of the soil, so that the roots can everywhere find a store of it."

R. Warington<sup>2</sup> and P. Richard<sup>3</sup> show that gypsum has also a favorable action in promoting nitrification in the soil.

According to Stockhardt, "the action of gypsum perhaps, more than any other manure, depends upon the kind of soil and crop, upon climate and other conditions, and is subject to manifold limitations."<sup>4</sup> In this connection it is of interest to note that in a number of recent experiments with this fertilizer, reports unfavorable to its use are given. L. L. Harter<sup>4</sup> reports: "In all our experiments gypsum has proven decidedly injurious to Norfolk soils and its use is not recommended." Morse and Curry<sup>5</sup> have made extensive studies on the effects of lime and gypsum

<sup>1</sup> "Storer's Agriculture," 1-207.

<sup>2</sup> *Trans. Chem. Soc.*, 47, 758.

<sup>3</sup> *Ann. de Chim. et de Phys.*, 25, 271.

<sup>4</sup> *Bull.* 1, Virginia Truck Exp. Sta.

<sup>5</sup> *N. H. Bull.* 142.

<sup>1</sup> 55 samples.

<sup>2</sup> 64 samples.

on some of the New Hampshire soils as well as upon samples of feldspar (apophyllite). They note little chemical effect in liberation of potash from the soils by either the lime or gypsum. From the feldspar the lime dissolved appreciable amounts of potash and about three times that released by the gypsum. They state it is because of the fixing action of the clay that the lime does not apparently increase the water-soluble potash in these soils.

In connection with some soil studies which have been carried out recently in this laboratory, the comparative reactions of lime and gypsum on a few typical soils have been investigated as regards the liberation of soluble potash by these fertilizers. The soils of this region are in general clay loams of basaltic origin and usually contain a good stock of potash. Soil No. 1, referred to in the following table, is a clay loam from the college farm and is typical of the southern portion of the Willamette Valley. Soil No. 2 is a bench land sample commonly characterized as "red hill" or "shot" soil and is a high-grade fruit soil. Soil No. 3 is a mildly alkaline silt loam from the branch experiment farm at Union. The composition of these soils with respect to potash is as follows:

TABLE I.—COMPOSITION OF SOILS IN POTASH.

	1. Per cent.	2. Per cent.	2. Per cent.
Total.....	2.77	1.09	1.18
Soil HCl 1.115.....	0.30	0.23	0.64
Soil HNO <sub>3</sub> N/5.....	0.035	0.038	0.145

In the first series of tests large glass percolators having a capacity of about twenty-five pounds of soil were filled with the soils which had been moistened to a good working condition with water (20–25 per cent.). The fertilizers were then applied and thoroughly mixed with the soil, the outlet of percolator closed with a cork, and the top of the soil covered with a layer of paraffine to prevent evaporation. After standing six weeks the corks were removed and the percolator leached with distilled water until approximately 500 cc. of percolate were obtained. The potash was then determined in these solutions by the method of Cameron and Failyer<sup>1</sup> and the colors read in a Schreiner colorimeter. Results of these tests are recorded in the following table:

TABLE II.—POTASH IN PARTS PER MILLION OF SOLUTION.

	Blank.	1 Per cent. CaO.	1 Per cent. CaSO <sub>4</sub> .
Soil No. 1.....	2.7	4.7	7.2
Soil No. 2.....	3.1	4.0	7.2
Soil No. 3.....	53.5	69.2	88.0

It is seen that both lime and gypsum increased the amount of water-soluble potash in these soils though the action of the lime is in some cases very slight.

Very little action was exerted by either agent on the water-soluble phosphates.

In the following tests the lime and gypsum used were specially purified potash-free in order that no soluble potash could be introduced in these reagents. Fifty grams of soil were treated in each case with 500 cc. of distilled water and one gram of lime and gypsum, respectively. The material was placed in stoppered bottles and shaken occasionally for twenty-four hours at room temperature. After filtration through a Pasteur-Chamberland filter an aliquot was analyzed as above, a blank with distilled water being run in each instance.

TABLE III.—POTASH IN PARTS PER MILLION OF DRY SOIL.

	Time. Hours.	Blank.	1 gram CaO.	1 gram CaSO <sub>4</sub> .
Soil No. 1.....	24	7.7	5.0	31.3
	96	....	5.6	....
Soil No. 2.....	24	14.0	9.2	37.4
Feldspar (pegmatite) .	24	32.3	22.5	51.7

In the above table it is seen that gypsum was pronounced in its action in each instance on the soil as well as the feldspar, while lime reduced slightly the amount of soluble potash. It is evident that gypsum acts as an indirect potash fertilizer on these soils while lime does not.

In some localities where plaster has been used for a long period of years it is claimed that the soil does not respond to its application as readily as formerly. One particular field, a sandy loam used for market gardening, has come to our notice, however, which has had applications of plaster for 25 years at the rate of 200 pounds per acre and still responds readily to this treatment. An examination of this soil together with the same soil in an adjoining field not treated with gypsum gave the following interesting results, tests being made of the surface nine inches of the soil in each instance:

TABLE IV.—PER CENT. OF POTASH.

	Unplastered soil.	Plastered soil.
Potash sol. in HCl 1.115.....	0.202	0.268
Potash sol. in HNO <sub>3</sub> N/5.....	0.050	0.069

These results indicate that considerably larger amounts of available potash are present in the soil which has been for a long period treated with gypsum.

## SUMMARY.

The soils of Western Oregon respond readily to applications of gypsum. Tests on a number of these soils with lime and gypsum under different conditions indicate that gypsum here acts as an indirect potash fertilizer while lime does not. Neither of these fertilizers affects the amount of water soluble phosphates in the soil.

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<sup>1</sup> Bur. Soils, Bull. 31.



## THE CHEMICAL COMPOSITION OF KAFIR CORN.

(FIRST PAPER.)

By R. O. BAIRD AND C. K. FRANCIS.

Kafir corn, *Andropogon sorghum vulgaris*, comes under the general classification of sorghums, and is supposed to have originated from a single species native to tropical Africa. It takes its name from the well-known Kafir tribe.

The value of Kafir corn as a drought-resistant crop has been clearly proved.<sup>1</sup> It can be depended upon for good yields under conditions distinctly unfavorable to Indian corn. Its value in the semi-arid regions of the United States cannot be overestimated as it is better able to withstand the drought and hot winds than any other crop. The hot winds may cause this species of plant to wither, but if favorable conditions follow a period of drought it resumes growth, and produces good yields. During the past few years a large acreage has been devoted to this

though its milling qualities are given more consideration to-day than ever before.

*Scope of the Investigation.*—In order to determine the value of the Kafir corn kernel as a food and as a raw product in manufacture the experiments herein reported were planned as outlined below:

1. A study of the chemical compounds which make up the proximate constituents of the Kafir kernel for a comparison with Indian corn.

2. The relation between the inorganic plant constituents of Kafir corn and Indian corn, and the approximate amount of plant foods removed from the soil by each.

3. A study of the Kafir corn fat and methods of extracting it from the seed.

## ANALYTICAL METHODS.

The samples of Kafir corn kernels were obtained from local dealers and from the Oklahoma Experiment Station fields. Sample No. 4764 was taken from a "no treatment" field while sample No. 4765 was taken from a plat which had been well manured. About one bushel of each sample was freed from hulls, thoroughly mixed and ground to a fine meal. The meal was quartered down to about 1 kilo and then placed in air-tight jars until analyzed.

*Moisture.*—The moisture was determined by drying five grams of the sample for 12 hours at 100°.

*Ash.*—The ash was determined by incinerating five grams of the sample until no loss of weight was noticed on further heating. The time required was about eight hours.

*Crude Fiber.*—This determination was made by the official method.<sup>1</sup>

*Ether Extract.*—The indirect method was used.

*Nitrogen.*—The Gunning method was used in this determination.

*Nitrogen-free Extract.*—Was determined by subtracting from 100 the sum of the percentages of moisture, ash, crude fiber, ether extract, and protein.

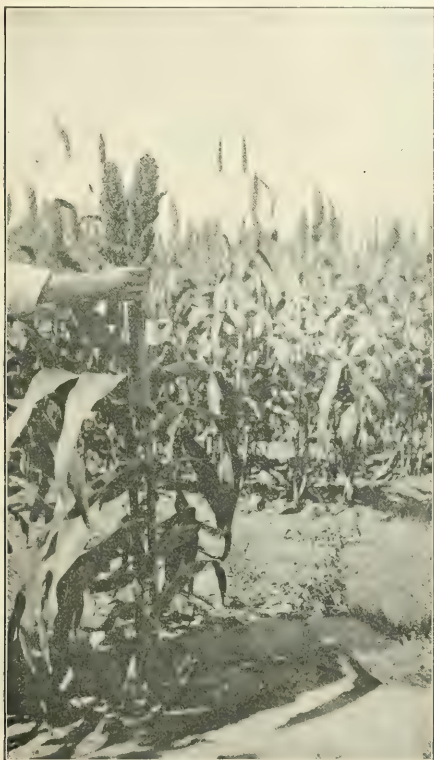
*Starch.*—This determination was accomplished by the direct acid-hydrolysis (modified Sachsse method). The diastase method for the determination of starch was tried several times, but the results did not agree, and were never high enough in starch.

Reducing sugars, sucrose, galactans, and pentosans were determined by the official methods.

*Specific Gravity.*—A 25 cc. gravity bottle was used in this determination. The weighings were made at 15.5°.

*Melting Point of the Fat.*—This determination was carried out according to the method proposed by Wiley. A flat disc, made by dropping the melted fat on ice, was heated in a mixture of alcohol and water. The temperature at which the disc rolled into a sphere was considered the melting point.

<sup>1</sup> U. S. Department Bureau of Chemistry, *Bulletin 107* (Revised), was used as a guide in all determinations unless stated otherwise.



Well developed Kafir corn.

crop and almost entirely for the purpose of producing roughage for live stock. The value of the grain as a food for stock and man is not fully appreciated,

<sup>1</sup> Oklahoma Agricultural Experiment Station, *Bulletin 87*, 1910.

**Solidifying Point—Titer Test.**—The method of Dali-can was used for this determination.<sup>1</sup>

**Iodin Absorption Value.**—Hübl's method for the absorption of iodine was used according to the official methods.

**Saponification Number.**—The method used in this determination was that of Koettstorfer.

**Acetyl Value.**—This determination was made according to Lewkowitsch.<sup>2</sup>

Soluble and insoluble acids, Reichert-Meissl number, free fatty acids, Maumené number and inorganic plant constituents were determined according to the well-known standard methods.

1. *Proximate Constituents of the Kafir Kernel.*—In order to show the relative value of the proximate constituents of the Kafir corn kernel, some standard must be chosen for comparison. As Indian corn, in conditions of growth and nature of environment, is somewhat similar to Kafir corn, it will be used for comparison.

TABLE I.—COMPOSITION OF KAFIR CORN.

Sample.	Moisture.	Ash.	Protein.	Fiber.	Nitrogen-free extract.	Fat.	Nitrogen.
3302 Kafir meal...	12.43	1.13	11.25	1.89	71.09	2.21	1.800
3804 Kafir meal...	12.63	1.28	11.47	...	71.83	2.79	1.834
3308 Kafir meal...	13.50	1.25	11.47	1.79	69.47	2.52	1.834
3367 Kafir meal...	13.46	1.23	10.60	1.86	70.80	2.05	1.697
3383 Kafir meal...	13.31	1.27	10.95	1.85	71.31	1.32	1.751
4122 Kafir meal...	12.02	1.26	10.06	...	73.72	2.94	1.610
4123 Kafir meal...	12.06	1.23	9.89	...	73.87	2.95	1.582
4720 Kafir grain...	10.08	1.40	9.19	2.15	74.31	2.87	1.477

TABLE II.—COMPOSITION OF INDIAN CORN.

Sample.	Moisture.	Ash.	Protein.	Fiber.	Nitrogen-free extract.	Fat.	Nitrogen.
3301 Cornmeal...	11.59	1.38	9.70	2.16	71.64	3.53	1.551
3803 Shelled corn...	12.56	1.23	9.63	...	72.96	3.62	1.540
3804 Cornmeal...	12.54	1.35	9.27	...	72.91	3.93	1.484
3307 Cornmeal...	14.58	1.28	9.71	2.03	71.40	1.00	1.553
3366 Cornmeal...	13.81	1.35	9.30	2.13	72.26	1.11	1.487
3382 Cornmeal...	13.03	1.47	9.74	2.13	72.30	1.33	1.558
4121 Cornmeal...	11.26	1.29	8.84	...	74.25	4.26	1.414
4706 Corn chops...	10.89	1.02	8.57	1.99	74.27	3.26	1.372
4716 Corn chops...	9.74	1.27	10.06	2.65	72.29	3.99	1.610
4717 Corn chops...	9.70	1.22	10.06	2.54	72.12	4.36	1.610

From the preceding analyses of Kafir corn and Indian corn obtained from different parts of Oklahoma, the conclusion can be reasonably drawn that Kafir corn is similar in composition to Indian corn and is therefore a valuable food. The analyses presented by Tables I and II show that the protein and carbohydrates in Kafir corn are slightly higher and the fat somewhat lower in per cent. than in Indian corn.

Samples Nos. 4764 and 4765 were taken from unmanured and manured fields, respectively. The effect of the fertilizer is apparent in every determination, and illustrates a remarkable response to the application of fertilizing material.

TABLE III.—ANALYSES OF KAFIR CORN.

Sample.	Moisture.	Ash.	Crude fiber.	Fat.	Protein.	Nitrogen-free extract.
4760.....	13.471	1.453	2.648	3.416	12.85	66.162
4762.....	12.250	1.196	2.470	3.541	12.97	67.573
4763.....	11.474	1.277	3.319	3.570	11.92	68.440
4764.....	12.805	1.599	2.957	3.517	11.06	68.061
4765.....	13.105	1.700	2.890	3.896	11.99	66.419
Maximum.	13.448	1.668	2.900	3.800	12.85	70.826
Minimum.	11.264	1.196	1.880	3.464	11.37	65.334
Mean	12.356	1.432	2.390	3.632	12.11	68.080

Table III shows that the proximate constituents of Kafir corn are fairly uniform, for the samples were obtained from various places.

In the following tables the results of a number of analyses have been averaged and calculated to moisture-free basis. The data for Indian corn is that reported by Dr. C. G. Hopkins.<sup>1</sup>

TABLE IV.—COMPARISON OF INDIAN CORN AND KAFIR CORN. MOISTURE-FREE BASIS.

	Indian corn.		Kafir corn.	
	Maximum.	Minimum.	Maximum.	Minimum.
Ash.....	1.74	1.09	1.93	1.35
Protein.....	13.88	8.35	14.85	12.81
Fat.....	6.02	3.95	4.39	3.90
Carbohydrates.....	85.78	78.92	84.33	76.44

The following table will show more clearly the comparison of the food constituents of Indian corn and Kafir corn:

TABLE V.—FOOD VALUES COMPARED.

	Kafir corn.	Indian corn.
Average yield per acre.....	30 bu.	35 bu.
Feeding value, considering corn 100.	90	100
Pounds of protein per acre, considering 11.3 per cent. of Kafir corn and 10.5 per cent. Indian corn...	219.84	205.80
Pounds of fat per acre, considering Kafir corn 3 per cent. and Indian corn 3.5 per cent.....	50.4	68.6
Pounds of nitrogen-free extract per acre, considering Kafir corn 70 per cent., Indian corn 72.5 per cent.....	1176.0	1421.0
Value per acre, considering corn worth 37.5 cents and Kafir corn worth 30 cents per bu.....	\$9.00	\$13.125

**Nitrogen-free Extract.**—Under this head is included the starch, glucose or dextrose, sucrose, galactans and pentosans. The determination of these compounds show more completely the value of the nitrogen-free extract.

The following table contains the results of the analysis of nitrogen-free extract:

TABLE VI.—COMPOSITION OF NITROGEN-FREE EXTRACT.

Sample.	Nitrogen-free extract.	Starch.	Pentosans.	Galactans.	Glucose.	Sucrose.
4760.....	66.162	59.484	3.92	0.240	1.375	0.275
4762.....	67.573	60.713	3.79	0.150	1.362	0.406
4763.....	68.440	59.031	4.41	0.136	1.360	0.493
4764.....	68.061	57.125	4.53	0.119	1.440	0.669
4765.....	66.419	57.956	5.04	0.104	1.345	0.795

From the preceding table the following conclusions can be reasonably drawn:

University of Illinois, Bull. 53.

<sup>1</sup> Food Inspection. Leach, p. 403.

<sup>2</sup> Jour. Soc. Chem. Ind., 503, 1897. Chemical Technology, Lewkowitsch, 1, 268 (1904).

<sup>3</sup> The results in all tables are expressed in per cent. unless otherwise indicated.

That Kafir corn kernel has as much sucrose, reducing sugars and pentose bodies as Indian corn. The analyses also show that 90 per cent. or more of the nitrogen-free extract can be utilized as a food.

The following table has been computed from Table VI, and shows the value of Kafir corn for the production of alcohol as compared with Indian corn:

TABLE VII.—PRODUCTION OF ALCOHOL.

	Kafir corn.	Indian corn.
Pounds of fermentable material (starch and sugars) in one bushel.....	38.0	39.2
Approximate pounds of alcohol per bushel.....	18.0	19.0
Gallons of alcohol in one bushel.....	2.56	2.7
Cost of grain <sup>1</sup> to produce one gallon of alcohol.....	12 c.	14 c.

2. *Determination of the Inorganic Plant Constituents.*—The ground meal was ignited in a muffle furnace and the charred material extracted with a 10 per cent. solution of acetic acid. The acid was washed out with hot water and the combined filtrates evaporated and burned to a white ash. The residue was also burned to a white ash, and the two thoroughly mixed and placed in ground-glass stoppered bottles until used for analysis.

In Table VIII complete analyses of the ash of Kafir corn are reported. The composition of the ash of Indian corn is shown in Table IX:

TABLE VIII.—ASH OF KAFIR CORN.

Sample number.	3898.	3958.	3230.	3231.	Average.
Sand.....	4.30	3.33	5.73	2.88	4.06
Soluble silica.....	0.96	1.28	2.25	4.15	2.16
Carbon.....	0.24	0.31	0.28	0.17	0.25
Sulphur trioxid.....	0.19	0.17	1.22	0.51	0.52
Chlorin.....	0.45	0.48	0.58	0.44	0.49
Sodium oxid.....	0.94	0.96	2.42	2.39	1.18
Phosphorus pentoxid.....	43.76	44.21	37.47	46.72	43.04
Iron and aluminum oxids	1.19	1.18	2.08	1.84	1.57
Calcium oxid.....	1.95	2.15	1.64	1.46	1.80
Magnesium oxid.....	18.86	18.56	16.67	15.25	17.34
Potassium oxid.....	27.11	26.99	29.78	24.82	27.17

TABLE IX.—ASH OF INDIAN CORN.

	By Wolff. <sup>2</sup>	By Ford. <sup>3</sup>
Potassium oxid.....	29.80	29.15
Sodium oxid.....	1.10	1.76
Calcium oxid.....	2.20	1.60
Iron and aluminum oxids.....	0.80 <sup>4</sup>	1.64
Phosphorus pentoxid.....	45.60	49.58
Magnesium oxid.....	15.50	13.29
Sulfur trioxid.....	0.80	0.54
Silica.....	2.10	2.45
Chlorin.....	0.90	0.66

From the above analyses it will be seen that 87.55 per cent. of the Kafir ash and 92.29 per cent. of the corn ash is in the form of potassium and magnesium phosphates. The average per cent. of ash in Kafir corn kernel is 1.433 while that of corn is 1.372.

The following table shows the approximate amount of potassium oxid, phosphorus pentoxid, and nitrogen, which is removed from the soil by an average crop of Kafir corn and Indian corn:

<sup>1</sup> Corn, 37.5 c.; Kafir, 30 c. per bushel.  
<sup>2</sup> Wolff's *Aschen Analysen*, 1880. See also Thorp's *Dictionary of Analytical Chemistry*, Vol. I, page 497, 1890.  
<sup>3</sup> Oklahoma Experiment Station.  
<sup>4</sup> Wolff reported iron oxid only.

TABLE X.—PLANT FOOD REMOVED FROM SOIL.

	Kafir corn.	Indian corn.
Average yield in bushels per acre.....	30.000	35.000
Pounds per bushel of potassium oxid.....	0.218	0.227
Pounds per acre of potassium oxid.....	6.540	7.945
Pounds per bushel of phosphorus pentoxid.....	0.345	0.366
Pounds per acre of phosphorus pentoxid.....	10.362	12.810
Pounds per bushel of nitrogen.....	1.089	1.023
Pounds per acre of nitrogen.....	32.940	35.798

As shown by the above table, corn takes up from the soil a larger quantity of the three important plant foods than Kafir. This knowledge is of special value when allowance is made for the fact that corn has been shown by analysis, to be very little, if any, better than Kafir corn as a feed for stock and poultry.

3. *Kafir Corn Fat.*—Equal quantities of five samples of Kafir corn kernel were well mixed, ground to a very fine meal and the fat extracted with gasoline. Large bottles were used in the extraction, and the mixture of meal and gasoline was shaken thoroughly every few hours. After standing for 24 hours the gasoline and the extracted fat were put into another bottle with a new charge of meal, and this process continued for five days, each charge of meal being extracted five times. The liquid was then filtered, evaporated, and purified.

In the evaporation of the mixture most of the gasoline was removed by the aid of heat and a suction, pump. The liquid was placed in 500 cc. Jena flasks attached to a suction pump, and the flasks placed in a bucket of water. The water was heated from 55° to 60° C., the suction started, and the process continued for 36 hours.

The golden liquid obtained from the gasoline extraction was poured into a flask (1000 cc.) and heated in a water oven kept at 100°. While the liquid was being heated carbon dioxide, which had previously been dried by means of calcium chlorid and sulphuric acid, was drawn through it. After 40–50 hours this treatment usually removed all of the water and any traces of gasoline.

The fat on cooling, became solid, not unlike vaseline, though somewhat harder. It had a yellow color with a greenish hue, a pleasant though not marked odor, and a pleasant vegetable oily taste.

TABLE XI.—CONSTANTS OF KAFIR CORN FAT AND CORN OIL.

	Kafir fat.		Corn oil. <sup>1</sup>	
	1.	2.	1.	2.
Specific gravity.....	0.9398	0.9397	0.9274	0.9213
Melting point.....	44.4°	44.0°	18.0°	20.0°
Titer test.....	34.1°	33.8°	14.0°	16.0°
Iodin value.....	109.98	109.43	111.0	180.0
Soluble acids.....	0.64	0.68	...	...
Insoluble acids.....	93.04	93.41	82.2	95.7
Saponification value.....	249.7	248.5	188.0	193.0
Richert-Meissl No.....	6.14	6.07	4.2	9.9
Liquid acids.....	86.44	85.52	...	...
Solid acids.....	7.40	7.55	...	...
Free fatty acids.....	26.93	27.10	...	...
Acetyl value.....	42.22	42.24	7.8	8.75
Maumené number.....	68.2°	68.0°	5.6°	8.6°
Unsatifiable res.....	1.72	1.71	...	...

<sup>1</sup> Chemical Technology, Lewkowitsch, II, 515, 1904.



In Table XI the chemical and physical constants of two samples of Kafir fat are compared with those of two samples of corn oil.

The melting point of Kafir corn fat is 44.2, and that of corn oil is 18° to 20° C. This and the higher Titer test of the Kafir fat shows that the latter contains more of the solid fatty acids than corn oil. The indications are that Kafir fat could be utilized much more satisfactorily than corn oil for soap-making. An experiment demonstrated that the fat could not be used as a lubricant owing to the high percentage of acids. The fat might, however, be used with other oils especially the edible fats and oils, as it has an agreeable taste and odor. Owing to its high melting point it might be used with such fats as lard, oleomargarine and butterine. The fat was found to be practically non-drying.

The fat is soluble in gasoline, ether, chloroform, carbon bisulphide, and to some extent in absolute alcohol. This property is receiving attention with more detailed consideration of the investigation.

#### SUMMARY AND CONCLUSIONS.

The proximate analysis shows the Kafir kernel to compare favorably with corn.

a. Kafir corn is more uniform than corn in composition.

b. It is a cheap food.

Alcohol and glucose can be produced cheaper from Kafir corn than from corn if the cost of the raw material is alone considered.

Kafir corn removes a smaller quantity of the important plant foods from the soil than corn. This fact has been shown by analyses of the ash of both grains which were grown under similar conditions.

The fat from the Kafir kernel is a solid which melts at 44.2°.

c. It should be valuable in the manufacture of soaps and fatty acid products.

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#### ADDRESSES.

#### PRESENT STATUS OF OZONE, WITH REFERENCE TO AIR PURIFICATION.<sup>1</sup>

By RALPH D. SMALL.

The development of ozone for industrial uses, water purification and ventilation, has progressed rapidly since 1903, which seems to be the median line between inaccuracy and accuracy so far as determination, concentration, economical operation, properties and uses of ozone are concerned. In 1890, the French Academy appointed a commission to report on the status of ozone in Europe. After a lengthy investigation their report submitted proved absolutely inconclusive. The members were almost divided as to what they recognized had been scientifically proven. From 1895 to the present date the whole subject has

<sup>1</sup> Read before the 18th general meeting of the American Electrochemical Society, October 14, 1910, at Chicago, Ill.

been largely taken out of the laboratory and put on a commercial plane, and this has been chiefly dependent upon the progress and developments that have taken place in the electrical industry.

As this paper is to be largely devoted to the uses of ozonized air as an adjunct or supplement to ventilation, very little reference will be made to the largest commercial use to which ozone has at present been put, namely—that of water purification, except to state that water purification by ozone has in many places in Europe supplanted every other method of filtration and sterilization that is known. In the United States, owing probably to imperfectly developed methods, a like success cannot be claimed. Schneller, De Fries, W. Siemens, Vosmaer, Becquerel, Otto, Ehrhwein, Gerard, Berthelot, Koch, Ohlmüller have all been largely responsible for the progress that has been made along this line. To-day there are over 40 cities and towns in France that are purifying all or part of their water supply with ozone apparatus. In Germany also this method is being rapidly adopted. Some idea may be gained of the efficiency of this method when, as is stated,<sup>1</sup> "ozone treatment reduced the bacterial count in water from 12 million to 40 with a total consumption of 18 grams of ozone per cubic meter." To-day there are over 150 patents in the United States Patent Office, and this department is rapidly becoming one of the "busy" departments, thus indicating the amount of interest that is now being taken in the latest development of the electro-chemical field. One of the former heads of the Westinghouse interest has been credited with the remark that "not only was ozone the coming thing in electricity, but was destined to be in the course of time one of the largest fields with which electricity would be identified, barring the use of light and power."

There are various ways of producing ozone, such as the oxidation of phosphorus, or the action of ultraviolet rays upon air, these rays being produced by a mercury vapor lamp in a quartz receptacle, or by heat, according to Nerst and Clement, by which they produce 3 grams per kilowatt hour. It should be stated here that concentration is the percentage of ozone usually measured in grams contained in a cubic meter (about 35 cubic feet) of air. All these processes, however, are not economical for commercial purposes. Ozone is produced in nature by evaporating water, when acted upon by the ultraviolet rays of either sunlight or electrical discharge. It is also produced from green plant life in what is known as the process of photo synthesis. In this process carbon dioxide is absorbed and unites with water to form carbohydrates. In this chemical reaction the atoms of oxygen are liberated and appear in a nascent state. This affords a logical origin for the presence of ozone in the vicinity of forests or where much plant life is found. Its presence in mountainous regions and higher air strata is largely accounted for, first—by the lack of organic impurities to use it up, and, second, because the sun's ultraviolet rays having less atmosphere to pass through are more slowly absorbed. This is investigated quite extensively by Ladenburg and Lehmann, as was noticed in the *Scientific American* of August 6th, and their works are now the basis of a series of investigations on the part of the United States Weather Bureau. The spectroscope is used to determine the presence of ozone in such investigations.

It is generally conceded now since the research of Henriot and Bouysey, and also Steinmetz, that ozone is created by the action of ultraviolet rays upon oxygen; that it is an endothermic process; heat is absorbed. In nature this usually takes place and is more observable when there is much electricity in the air, or when water evaporates quickly as on the beach of the seashore, where it is in a finely divided state, and on account of which these rays have a better opportunity for their peculiar action.

<sup>1</sup> *Engineering News*, April 28, p. 497.

For air-conditioning purposes ozone is now being made with generators, which first change the direct current to an alternating current, preferably with cycles not less than 60, and then step-up the voltage to 5,000–30,000, although it is now thought that to obtain the best economies a voltage under 8,000 is poor practice. The discharge is made by electrodes on either side of a dielectric, such as glass, micanite, mica, or some high insulating material, there being an air gap between the dielectric and the electrodes. The electric glow, which has no sparks such as is exhibited in the voltaic arc and which is comparatively heatless, is a brush discharge, purple in color, and fairly quiet in its action. Various types of condensers and electrodes have been used from 1859 down to date. The consensus of modern opinion is that point electrodes such as employed by Andreoli and others have disadvantages, first, because they quickly lose their pointed character and round off, or, second, because a minute particle of dust can do a great amount of destructive work on a small point, in generating heat and interrupting the flow of electricity. Third, because the necessary cleaning of an infinitely large number of points require too much attention. Leon Gerard, one of the leading electrical engineers of Belgium, states: "The aigrette or point electrodes apparatus has only 55 per cent. efficiency of those where the glow discharge is used." Other types of electrodes are either plates or cylinders on either side of a dielectric material, and these appear in various forms—flat, serrated, gridded or perforated. Another type is the covered electrodes, with no metal exposed, which is very commendable. A fourth is the use of a rotating fan electrode, such as is shown in the Vohr type, which has the advantage of quickly forcing the air through the generating field, and ozonizing it at the same time, thus giving a high purity of product. It is generally regarded as axiomatic that the briefer the period of ozonization the purer the resultant gas, purity meaning practically an absence of oxides of nitrogen, which are principally produced by heat, sparking, or the presence of dirt.

The amount of nitrous oxide generated by any properly made type of air ozonizer, however, is so infinitely small that it can be totally disregarded. This statement, however, does not apply to all ozonizers, as will be later explained.

It may be stated: The more modern machines consume in operation 40–250 watts per hour.

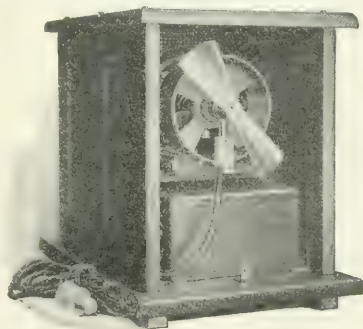
Normal air has as its constituents, according to recent tables, giving volumes per 1,000 and not using the decimals beyond the 4th place:

Nitrogen .....	769.0
Oxygen .....	206.0
Aqueous vapor .....	14.0
Argon .....	9.0
Carbon dioxide .....	0.33
Hydrogen .....	0.19
Ammonia .....	0.008
Ozone .....	0.0015
Nitric acid .....	0.0005

This is for normal air. It does not apply to air where all the ozone has been used up in oxidizing such various substances as the exhalations and emanations from millions of human beings, horses, automobiles, smoke from factories, trains, boats, gases and dust from manufacturing processes, volatile substances from rendering plants, packing houses and decomposing garbage and refuse in the street.

Authorities differ as to the amount of ozone in the air. It has been given all the way from one part in one million by volume up to one part in 20 millions. Perhaps a figure from 1 in 1,000,000 to 1 in 5,000,000 would represent what most have agreed upon as correct for those places where the presence of ozone is easily detected, so that the best constructed ozonizers of later years have been in alignment with, or very little in excess of, the concentration which nature provides in localities remarkable for their invigorating air. German scientists have

stated: "1/10 of a mg. to 1 mg. as the ideal concentration for continuous breathing." The limits as recommended by recent investigators is somewhere between 1/10th of a mg. up to 2 mg. If a density of much over a centigram is used, another factor must be relied upon to dilute the ozone to a point where it is agreeable to breathe, that is, the rest of the air in the room. This is unscientific, because you are dealing with a factor out-



Vohr ozonizer.

side of your own control, and the air currents of any room differ from those of every other. The machine that delivers the ozone with a continuous uniform concentration and with a controllable yield is built along sane, scientific lines.

*Properties of Ozone.*—Ozone can be condensed to a liquid state of a bluish color, with a specific gravity of 1.46. In this state it boils at about 120° C. Its density is 1<sup>8</sup>/<sub>10</sub> as compared with oxygen, and 1<sup>66</sup>/<sub>100</sub> as compared to ordinary atmosphere. It is slightly soluble in water and more soluble in certain oils. It reverts to oxygen at 270° C. It is unstable and rapidly disintegrates on standing. The loosely attached third atom is constantly tending to fly off and combine with other atoms, as it has a remarkable affinity for all carbon or compounds of carbon, which so far as ventilation is concerned will be hereafter referred to as organic matter. Its value as an oxidizing agent is due to ease of application and because nothing but oxygen is used in reaction. In the lighter concentrations its odor faintly resembles that of freshly bleached linen and is crisp, refreshing and exhilarating. It can be detected by the nose when present in one part to 10 millions of air. In the higher concentrations its odor is pungent, heavy and disagreeable. Many of the properties of ozone are discussed in the works of Pescheux, Gerard, Le Caux, Warburg, Mendeleef, Berthelot, Ehrlein and Dr. Fischer of Germany. Heat and humidity are unfavorable conditions for the generation of ozone (see L. Gerard's treatise in the August, 1909, number, of *Société of Belgian Electricians*). For this reason different methods have been employed to keep the electrodes cool. Steynis uses ammonia gas in pipes. Gerard uses oil. Others employ water jackets. The preferable method for air purification is the rapid passage of air by suction pumps or fans, such as are found in the Siemens & Halske later models in Germany, and the Vohr model in the United States. Any type of ozonizer where no mechanical means are provided for forcing the air rapidly past the electrode surface is utterly unreliable. In the first place, the air will remain for too long a period in the heat zone and thus produce an unsafe amount of nitrous oxide. Furthermore, this type of generator is unscientific, as there are no means of obtaining either concentration or yield, since there is no regular air flow to measure by. You must guess at what is being made and how much of it. The amount of ozone generated is in direct proportion to the wattage of discharge per unit of air ozonized. Some element of heat is present in the so-called

"cold" discharge, and this tends to destroy a portion of the ozone generated and also destroys the theoretical accuracy of the above statement. Heat increases as the square of the current of discharge. It is therefore desirable to use a high voltage and low amperage, and it has been found that from 8,000-12,000 volts produce ozone with commendable economy.

Very high concentrations are needed for such purposes as water purification, the bleaching of fabrics, the destroying of disease germs, treating of petroleum oils, cyaniding (where with ozone it is now possible to get 94 per cent. efficiency off the plates where in many instances only 60 per cent. was obtainable before), sterilizing infected rooms, ships, etc. For all of the above from 1 up to 12 grams is required. As high as 30 grams concentration has been obtained. High concentrations necessitate high wattage of electrical discharge per unit of air. Here the air passage must be slow, which of course results in low volume of ozonized air. The converse of course holds true that the more rapid the air flow the higher will be the volume of ozonized air but the lower the density or concentration. For all these large concentrations it is better to dry the air by the use of quicklime or other means, but for ventilating purposes it is not necessary to resort to this in the more recent types of ozonizers. One of the objections to extraordinary humidity is that an infinitely small amount of peroxide of hydrogen is liable to be formed.

*Method of Measuring Ozone.*—The determination of the quantity of ozone generated is frequently obtained by using iodide of potassium solution. The iodine is freed by ozone, is acidified, then titrated by sodium thiosulphite and starch.

*Air Purification.*—Of all known subjects which are intimately connected with our health and working efficiency, the least understood, the least attended to, with the most widely varying opinions in regard to it, is the subject of air purification and the chemistry of the air we breathe. 20 years ago we would have complacently taken any kind of water from any spigot or hydrant without much thought. To-day you don't take that chance because you know it is a chance that may produce harm. We now have spring water in bottles in our offices, or we use boiled or filtered water at home. 20 years ago we took any kind of food in tin cans that was handed us at the grocery store, but to-day the laws of the United States protect us. Pure Food laws have materially cut down the ptomaine poisoning, dysentery, and various complaints arising from diseased or adulterated food. At present, however, although we eat but three times a day and drink water 7 or 8 times, we are breathing continuously both night and day and are thoughtlessly taking into our system any kind of air that we happen to find.

What is the harmful part of bad air? The consensus of modern chemists, physicists and scientists on this subject is absolutely conclusive, it permits of no debate. Experiments have been tried, tests have been made, and the old bugaboo—carbon dioxide—has been effectually exposed. Many persons used to entertain an idea which is rapidly becoming obsolete—that is, that the carbon dioxide in the air is the particular thing that creates the harm. Carbon dioxide is harmful *only* in that it *reduces the oxygen supply* by displacing it. As long as you can get the proper percentage of oxygen in the air that you breathe, the amount of carbon dioxide produced in any chemical laboratory can be present—according to the best scientists of the last ten years—to an amount of 20 times that which many engineers put as a figure destructive to life. Carbon dioxide is not poisonous, but when present in quantities in any air it is a danger sign that impurities exist in that air. But remember that it is a *sign board* and not the danger itself. It is the organic impurities exhaled at the same time as the carbon dioxide that are poisonous, so merely getting rid of carbon dioxide is a good deal like burning up the danger sign to get rid of the danger.

Dr. Ira Remsen, President of the Johns Hopkins University, of Baltimore, has done much to expel this carbon dioxide theory. He states: "Carbon dioxide is given off from the lungs just as it is from the fire. It is a waste product—it is not poisonous any more than water is. If, however, pure carbon dioxide is introduced into air it has been found that as much as 5 per cent. may be present without serious results to those who breathe it. The ill effects of breathing the air of a badly ventilated room occupied by a number of human beings appear to be due for most part to the presence of the small quantities of decomposing organic matters which are given off with the carbon dioxide and other gases. These act as poisons."

In "Air and Life," by Henry de Varigny, M.D., Sc.D., member of the Société de Biologie and Demonstrator of Museum of Natural History of Paris. "The atmosphere of a room may be considered vitiated as soon as it begins to smell close. This is not due to carbonic acid, which is scentless, but to organic impurities from the skin, mouth, etc."

Prof. S. H. Woodbridge, in Connecticut School Document No. 13, 1908: "The most active and dangerous impurity in the air of occupied enclosures is the matter of organic nature, thrown off by the body through its pores. That matter rapidly changes in character, passing through a fermenting and decomposing to a putrescent condition. The longer it is retained within a room the worse its odor becomes and the more morbidic its condition."

Organic impurities come from a variety of sources as has been previously mentioned. In all confined spaces, however, the chief source of air pollution is the organic matter cast off through the pores of the skin and the nose, throat and mouths of the individuals occupying that space. The longer that matter which the body has cast off remains suspended in the air the quicker it deteriorates. When it reaches a putrescent state it is unfit to be rebreathed. This is air sewage, and is just as unfit to take into the system as diseased meat would be unfit for the stomach. What our body has cast off it is safe to assume is unfit for further use. This organic impurity has recently been called "crowd poison," according to Dr. Fischer in "Ozone and Air Purification." He states: "What is known as 'crowd poison' is responsible for many of the bad air diseases. A large amount of decomposition is continually going on upon the surface of the body and in the nose, mouth and throat of every individual, so that large quantities of these 'decomposing products' are thrown out into the air. As these substances are formed more rapidly when there are a number of persons confined to the same space, they have been called 'crowd poison.' Wherever there is decay there is bound to be odor, and the unpleasant smell in confined spaces is due to this 'crowd poison.' 'Crowd poison' because of its odor also produces *shallow respiration* with the decreased oxygen supply which this occasions. It also has an effect upon the cell tissues in retarding proper oxidation. When the body cells are not properly oxidized or do not properly take the oxygen from the hemoglobin (which is that part of the blood which carries the oxygen to the tissues), we have more than enough of this hemoglobin. It is a general law of nature that what cannot be used is destroyed, so that we soon have a reduction in hemoglobin and *anemia* results. With the progress of anemia other disturbances manifest themselves. Without sufficient oxidation the fires of life begin to smolder. Food is not properly digested or assimilated. Mal-nutrition ensues and the weakened body easily falls a prey to any disease. *Prevention is better than cure*, and ozone, by destroying air poisons, does prevent the diseases which follow upon bad air."

So that it would seem that while ventilation is necessary to bring in out-of-door air to replace the oxygen which our breathing uses up, outdoor air alone is absolutely insufficient to purify the indoor air. It never did and never will *destroy* the im-



purities that constitute the danger element. Nature purifies her atmosphere with ozone. Man can purify it only with ozone. In "Atmosphere in Relation to Human Life and Health" F. R. Russell, Member of the Royal Institute of Great Britain, and Fellow of the Sanitary Institute, says: "Ozone is an important constituent of the atmosphere, greatly contributing to its purity and freshness and to the vigor of human life. Its activity is so great and its function so beneficial that its presence in normal quantities is a fair guarantee of the purity of the air and of health conditions. No ozone is found in the streets of large towns, and in most inhabited rooms, near decomposing matter, and in confined spaces generally."

Nothing has been said about ozone as a deodorizer. Its properties are remarkable in this line, and with higher concentrations almost any odor known, excepting the extraordinary perfumery from the pole-cat, can be successfully combated. In an office, factory or home the chief odors to be eliminated come from tobacco smoke, cooking, laundry, sick rooms or any overcrowded spaces.

**Therapeutics.**—It now seems to be regarded as an accepted opinion that colds and kindred diseases come from bad air, chiefly because bad air disturbs that part of the nervous system which regulates the blood circulation, and local blood congestion ensues, bringing with it an interference with certain bodily functions which destroy the bacteria constantly taken into the system. Thus infection occurs, lowering resistance to disease, and we start with colds, which are frequently the forerunner of tonsillitis, bronchitis, pneumonia, and even tuberculosis. Sir Frederick Treves, one of the four leading physicians of Europe, recently stated: "The idea that colds are caused by drafts is absurd. No cold ever had such an origin. Colds are a result not of drafts, but of stuffy rooms."

Undoubtedly ozonized air acts as a preventative of conditions which bring about many of our colds, and it is on the preventative rather than on the curative side that it has a serious claim to your consideration. There is just as much and no more magic in ozone for continuous breathing purposes as there is in pure air. Pure air will help the body to cure itself, and that is all that ozonized air in a concentration proper for breathing will do. There are so-called "doctors' machines," from which the patient is supposed to inhale ozone passed through turpentine oils for a few minutes each day. Nothing will be said about such apparatus except that it stands to reason that you cannot be sent to the Adirondacks, or Martha's Vineyard, or the Rocky Mountains and breathe that air for half an hour, and then be sent back home with any reasonable expectation that half hour's breathing will materially change your state of health. Interrupted administrations of ozone in high concentrations certainly cannot be seriously considered as beneficial as its continued use in more diluted and diffused form.

Dr. Oscar Linder said in a paper read at the Convention of American Institute of Chemical Engineers, June 24, 1910: "It is well known that this matter we have defined as air sewage is a specially attractive ground for bacteria, miasmata, and other animal and plant life of the lowest order, which thrive in cities and congested districts. In such small concentrations as ozone is employed in ventilating, the destruction of this air sewage is probably its beneficial action rather than the direct destruction of bacteria, which has sometimes been accredited to it. It has been proven that ozone, when diluted, to the extent of one part in one million parts of air, cannot act directly as a bactericide, but it is an established fact that even in such dilutions it acts as a deodorizer and destroyer of the food and favorite surroundings of the bacteria, thus depriving them of the conditions favorable to their propagation."

This is confirmed by D. Mendeléeff, in his "Principles of Chemistry, 1905," when he says: "The air of dwellings contains no ozone, the air of fields and forests always contains ozone;

that misamata, etc., are destroyed by ozonizing the atmosphere."

Abroad ozone as an air purifying agent and as a supplement to ventilation has been extensively used in factories, theatres, mines, ships, schools, hospitals, hotels, restaurants, gymnasia, offices, cold-storage houses, libraries and homes. The use of ozone in the purification of air is undoubtedly one of the most valuable of the newer achievements of electrochemistry.

## PLANT AND MACHINERY.

### THE TOOEELE SMELTER.<sup>1</sup>

By C. H. REPETH AND A. G. MCGREGOR.

The Tooeele smelter is situated about four miles east of Tooeele City, Tooeele County, Utah, and by rail is forty-one miles from Salt Lake City. The smelter is connected by its own railroad (the Tooeele Valley Railway) with the San Pedro, Los Angeles & Salt Lake railroad, the junction being about seven miles from the smelter site. The smelter is located upon a hillside, which makes it possible, to a large extent, for the level of delivery of the product of one building to be the level of charge floor of the next succeeding one.

**The Ores.**—The ores treated come principally from the mines of the Utah Consolidated Mining Company in Bingham Canyon. These mines in Bingham Canyon are connected with the smelter by an aerial tramway, four miles long, having a capacity of 125 tons per hour. Custom ores from other mines are received over the San Pedro railroad and the Tooeele Valley Railroad.

**Receiving Bins.**—The receiving bins are constructed of steel and are fire-proof throughout. The receiving bins have a capacity of 10,000 tons of ore and coal. The bins are so located and arranged that they may be served either by the 50-ton electric larry cars, which deliver the ore from the tramway terminal, or by standard railroad cars.

**Sampling Mill and Crushing Plant.**—This building is of steel and concrete throughout. It is 40 ft. x 84 ft. in plan, and is five stories high. The mill is composed of two sections, and each section has a crushing and sampling department. The ore from the receiving bins is automatically fed upon belt conveyors which convey it to shaking grizzlies that discharge the coarse ore into the crushers. The ore from the crushers is elevated to the top of the building by bucket elevators. In the sampling department the ore is cut four times by Brunton automatic samplers, cutting one-fifth of the amount each time and discarding four-fifths, so that of each ton of ore crushed a sample weighing 3.2 pounds is obtained.

The sampling department of each section of the mill contains, besides a 12" x 24" Blake crusher, which is common to the crushing and sampling department:

- 1 O-A sampler.
- 1 20" x 10" crusher.
- 1 1-A sampler.
- 1 48" x 12" rolls.
- 1 2 A sampler
- 1 26" x 15" rolls.
- 1 4-A sampler.

The discard from the sampling machines drops into screens of the crushing department, from which it is conveyed to the roaster bins. The final sample is quartered by a quartering shovel, the resulting sample is then dried on a steam drier, ground in an Englehardt sample grinder, and again ground in a Braun pulverizer, so as to pass through a 100-mesh sieve. The 100-mesh product is put up in three sample packages, one of which goes to the smelter laboratory for analysis, one to the

<sup>1</sup> Paper presented to the Utah Society of Engineers by C. H. Repeth, Superintendent Construction and A. G. McGregor, Electrical and Mechanical Engineer, Sept. 16, 1910.



Fig. 1.—General view of plant.



Fig. 2.—General view of plant.

owner of the ore, and one is filed away for use in case of a dispute.

The crushing department of each section of the mill contains:

- 1 12" x 24" Blake crusher.
- 2 15" x 9" crushers.
- 2 48" x 14" screens.
- 2 48" x 12" rolls.

From the crushing plant the crushed and sampled ore is conveyed by belt conveyors to the McDougal roaster steel receiving bins, which have a capacity of 5,700 tons. If it is desired, the coarse ore, after being sampled, may be conveyed to the blast furnace steel receiving bins, which have a capacity of 3,500 tons.

A blast furnace has not yet been installed, but provision has been made for it.

**Roaster Plant.**—From the roaster ore bins the ore is automatically fed upon a conveyor system which conveys it up to and discharges it directly into the McDougal furnace charge hoppers. The ore in transit from the bins to the roaster plant passes over a Blake-Denison automatic and continuous weighing and recording machine, which accurately weighs all the ore delivered to the roaster plant.

The roaster plant consists of two buildings, each 64 ft. x 162 ft. Each building contains sixteen McDougal calcining furnaces, of the Evans-Klepetsko type. These furnaces have

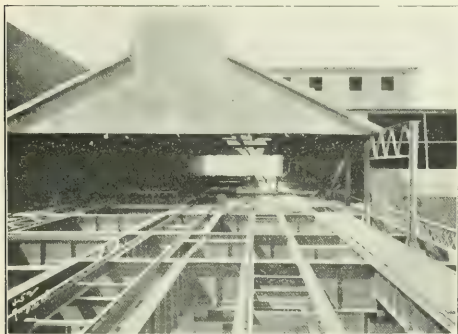


Fig. 3.—Reverberatory charge tracks.

six hearths 16 ft. in diameter and are 18 ft. high. They have revolving water-cooled shafts and arms, driven by a suitable gearing from the bottom. The rabbles are so set as to move the material from the circumference to center and *vice versa* on alternate hearths, until it finally drops into the calcine hoppers, immediately over the tracks of the electric tramming system, for transportation to the charge floor of the reverberatory building. No fuel is used other than the sulphur in the crushed ore, the burning of which furnishes sufficient heat to do the calcining. The gases are taken through flues into the large brick and steel dust chamber, which is 120 ft. x 140 ft. x 40 ft. high. This dust chamber is so arranged that the bottom forms a series of hoppers. The entire content of the dust chamber can be drawn into flue dust cars of the electric tramming system, and conveyed directly to the reverberatory furnaces for smelting. Each of the thirty-two McDougal furnaces has an approximate capacity of 45 tons in twenty-four hours.

**Reverberatory Plant.**—The reverberatory plant consists of three buildings joined together: the reverberatory charge building, containing the ore and coal hoppers over the furnaces 66 ft. x 280 ft.; the reverberatory furnace building, covering the larger portion of the furnaces, 82 ft. x 280 ft.; and the boiler house, 36 ft. x 326 ft. The latter at the present time contains four 746-horse power waste heat boilers and three 300-horse

power hand-fired boilers. The boilers are all of the Stirling water-tube type. The reverberatory plant contains five coal-fired reverberatory furnaces, the hearth dimensions of which are 19 ft. in width by 102 ft. in length, with a grate area of 7 ft. x 16 ft. These furnaces have a maximum capacity of 300 tons of calcine in twenty-four hours, on natural draft. The fuel



Fig. 4.—Ore car.

used is Diamondville coal, shipped from the mines in Wyoming owned by the Washoe Copper Company. The coal is dumped from large railway coal cars, or from cars of the electric tramming system, into hoppers that have five points of discharge, directly over the fire-box. The flame after leaving the furnace passes through a 746-horse power Stirling boiler, which reduces the temperature of the gases going to the main flue to about 600° F. By this means approximately 600 boiler horse power are obtained from each furnace from the waste heat. The ashes from the furnace fire-box fall into hopper cars of the electric tramming system, and are hauled away to the ash dump. The slag is skimmed from the reverberatories twice in eight hours. It is allowed to accumulate until its depth is from three to four inches above the skimming plate in the front of the furnaces, and then skimmed into slag cars having a capacity of 225 cubic feet, which are hauled to the slag dump over the electric tramming system. The matte is tapped from the side of



Fig. 5.—Main building.

the furnaces through a copper tap hole plate, and run through cast-iron launders directly into the converter building.

One of the waste-heat boilers referred to above has been equipped with a superheater. The superheater is just at the rear of the boiler. In case it proves satisfactory the other waste-heat boilers can each be equipped with one.



**Converter Plant.**—The main converter aisle of this plant is 65 ft. x 408 ft.; and the casting shed is 52 ft. x 255 ft. The main converter aisle contains five converter stands for 96" x 150" converters, and the converter lining department. The

ing plant. The product of the pug mill drops directly into a bin over the electric tramping system, from which it is transported in cars to the converter lining plant. The lining plant at the converter contains a 7-ft. grinding and mixing pan.



Fig. 6.—Blast furnace bins at left. Sampling and crushing plant in centre. Roaster ore bins at right.

converters used are of the horizontal barrel type, and are 96 inches in diameter x 150 inches in length. The converters are electrically operated. The main aisle is served by one 60-ton electric traveling crane. The casting department is served by a 30-ton electric traveling crane. As stated previously the matte is received in launders directly from the reverberatory furnaces. The end sections of these launders are pivoted, so that the matte may be poured directly into the converter opposite a reverberatory furnace, or the launder may be turned so that the matte will fall into a ladle, and be transferred to any of the other converters in the building. The slag from the converters is poured into unlined cast steel ladles, and transferred to the reverberatory furnaces by means of overhead cranes. There are two of these cranes, of 12.5-ton capacity each. The blister copper is poured into a ladle and transferred by the crane and transfer car to the casting department. In the casting department the ladle is handled by a crane and its contents emptied into anode moulds, which completes the operation of producing pig copper. The pig copper contains 99 per cent. copper and the gold and silver. It is shipped East, where it is further refined and the gold and silver extracted.

**Converter Lining.**—The converters are lined in the main converter building, but the lining material is prepared in a building 24 ft. x 40 ft., adjacent to the ore-crushing plant and receiving bins. The lining material contains a high percentage of silica, having gold and silver values. The material is crushed by the crushers in the crushing plant, and conveyed to a 7-ft. dry pan and pug mill, in the clay and silica mixing and grind-

ing plant. From the grinding pan the material is transferred to the converter, where it is tamped around a cast-iron form by a special Ingersoll-Sargent tamping machine, 5 inches diameter 20-inch stroke. The tamping machine is supported by a re-



Fig. 7.—Power plant.

volving jib crane, the vertical motion of which is controlled by an electric hoist. After lining, the converter is removed to its stand, where it is dried.

**Smelter Power Plant.**—The smelter power plant building is of brick and steel, the main aisle of which is 52 ft. x 240 ft.

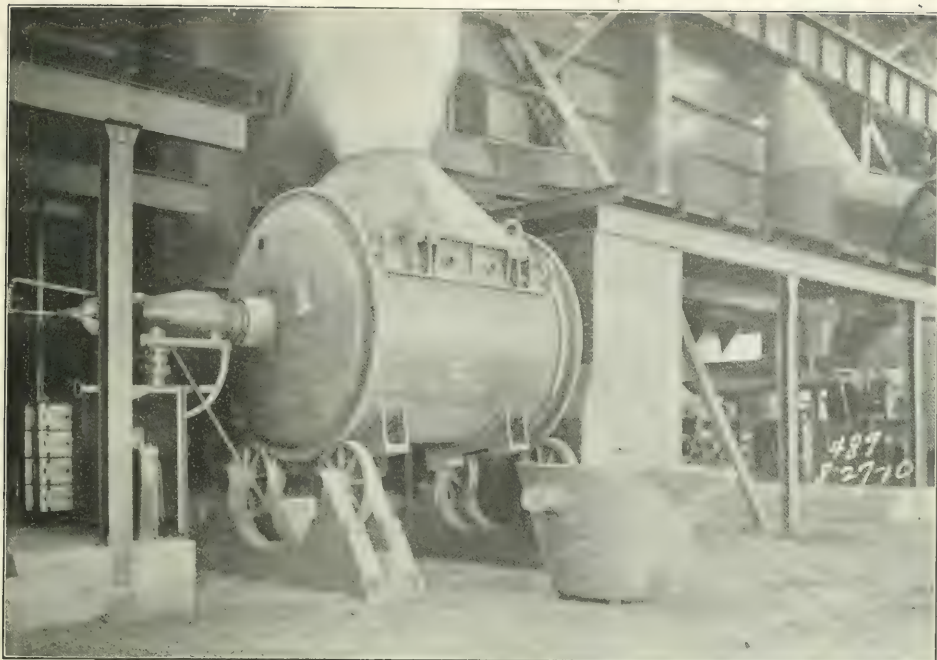


Fig. 8.—Blowing converter.



Fig. 9.—Skimming first converter at plant.

It has a lean-to 30 ft. x 90 ft. for the steam auxiliaries, and one on the other side 30 ft. x 60 ft. for the switchboard and transformer. The building contains the various power engines, blowing engines, compressors, and auxiliaries, and is equipped with an overhead electric traveling crane.

- 1 Engine-driven 50 kw. exciter generator.
- 2 Feed pumps having a total capacity of 678 gallons per minute.
- 1 Fire pump of 750 gallons per minute.

Besides the above, the plant contains the necessary condensers, vacuum pumps, feed-water heaters, traps, etc. The steam

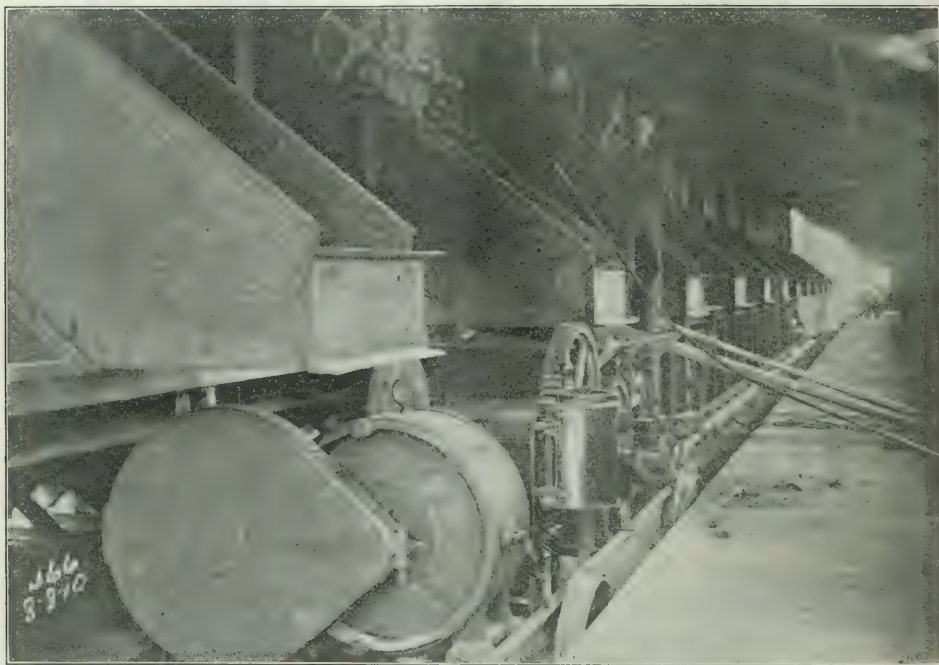


Fig. 10.—Conveyor feeding machine.

The building contains:

- 1 16" x 32" x 36" Corliss engine direct connected to a 250 kw. 500 volt D.C. generator.
- 1 15" x 30" x 36" Corliss engine direct connected to a 250 kw. 500 volt D.C. generator.
- 2 18" x 26" and 40" x 24" vertical triple expansion engines, each direct connected to one 750 K.V.A. 2200-volt generator.

for these engines is furnished by the waste-heat-boilers and hand-fired boilers adjacent to the reverberatory building.

The engine-driven generators, in addition, to furnishing power for the various motors about the plant, will also furnish power for driving air compressors and for hoisting and pumping purposes at the mines of the Utah Consolidated Mining Co.

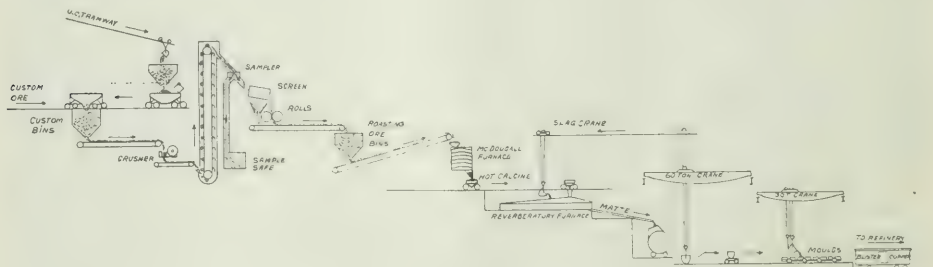


Fig. 11.—Diagram showing flow of material through Tooele plant.

- 1 15" x 30" x 36" x 42" blowing engine.
- 1 26" x 52" x 32" x 48" blowing engine.
- 1 13.5" x 26" x 26" x 15" x 36" steam-driven air compressor.
- 1 26.25" x 15.25" x 18" motor-driven air compressor.
- 1 200 kw. motor-driven D.C. generator.
- 1 50 kw. motor-driven exciter generator.

A cooling tower of the natural draft type has been constructed for cooling the water from the power plant condensers, and for cooling the cooling water for the McDougal roasting furnaces. The tower is 49 feet high, and at the base is 20 ft. wide by 140 ft. in length.



*Electric Trammimg System.*—The equipment of the electric trammimg system consists of:

3 7.5-ton and 2 18-ton electric locomotives.

50 cars of various kinds for handling ore, coal, calcine, flue dust, ashes and slag.

There are about ten miles of industrial tracks in the plant.

*Flues and Stack.*—The main flue which conveys the gases from the reverberatory furnaces and converters is 20 ft. wide by 18 ft. high and 1360 ft. long. One section of the converter flue is 8 ft. wide by 12 ft. deep, and 248 ft. long; the other section has a cross-sectional area of 132 ft., and is 181 ft. long. Both sections are provided with hopper bottoms and chutes for removing the flue dust. The roasting plant flue is 16 ft. x 16 ft. and is 255 ft. in length. The main and roasting plant flues are rectangular in section and of brick and I-beam construction, while the converter flues are constructed entirely of steel.

The stack is 25 ft. inside diameter at the top by 350 ft. in height above the base.

*Offices, Shops, Etc.*—The offices and shops are located in steel frame buildings, the outsides of which are sheathed and covered with corrugated iron. The office rooms are lathed with expanded metal and plastered on the inside. The main building is 74 ft. x 348 ft. and at one end are located the offices; at the other end of the building the machine, carpenter and electrical shops are located. Between the shops and office end of the building are located the warehouse, change rooms and laboratory. The blacksmith shop and boiler shop is located 180 ft. away from the machine shop. It measures in plan 74 ft. x 117 ft. Adjacent to the blacksmith and boiler shops is located the locomotive shed, which is 42 ft. x 89 ft. The locomotive shed houses the locomotives and spare electric trammimg equipment.

*Water System.*—The water for various purposes in the smelting plant is obtained from Pine Canyon. The water is conveyed by gravity from a dam in the canyon through a 12" pipe, approximately 5,000 ft., to a standpipe of 50,000 gallons capacity at the plant. The water is distributed from the standpipe to the various departments.

Two tanks having a capacity of 43,900 gallons each are located at an elevation such that ample pressure is afforded for fire purposes at any part of the plant. Water is pumped into these tanks from the general water supply by the fire pump at the power plant.

## NOTES AND CORRESPONDENCE.

### *Editor Journal of Industrial and Engineering Chemistry:*

In the October number of *THIS JOURNAL*, page 426, I note comments made by Mr. Fred C. Weld regarding "Accuracy in Sampling," referring particularly to the paper written by me some time ago.<sup>1</sup> I believe that more benefit would be derived to the readers of the *Journal* if there was more discussion upon subjects of interest and commercial value, especially one which is so important as that of securing representative samples of coal. However, as Mr. Weld's article takes the tone of criticism, rather than discussion, I think a little explanation will assist straightening out the points in question.

Mr. Weld's criticism appears to cover four points, as follows: first, error in calculations made from United States Geological Survey data; second, the application of the law of probability to errors in sampling coal; third, insufficiency of 1300 experiments; fourth, coinage of new words.

With reference to the data from Professional Paper No. 48, United States Geological Survey, which was used in my original paper, I merely averaged the percentage of ash in the various samples taken from the car, as well as from the producer, steam, and coking plants, giving each an equal weight, and stated that

this method was not absolutely correct. Mr. Weld has attempted to recalculate these results, multiplying the weight of coal used on the various tests by the percentage of ash determined from a sample of it, but he has encountered the same difficulty which I did originally, due to the fact that the entire amount of each car was not tested or resampled at the various plants. The method which I pursued, however, gave the Survey figures the benefit of the doubt, and did not show errors of as large a degree as do those determined by Mr. Weld with his method. In the case of the Iowa coal which Mr. Weld cited, he averages the three quantities delivered to the different plants according to their weight, and gets 16.17 per cent. ash. This is then averaged with the car sample, which was taken from the entire car as it was being unloaded, giving a final average of 15.69 per cent. He states that the error due to sampling was 0.47 per cent. In order to arrive at this conclusion, Mr. Weld assumes that each of the three samples taken at the steam, producer, and coking plants absolutely represented the coal which was delivered to each place, and that all error in sampling existed in the sample taken from the car as it was being unloaded. While there may have been some variation in the true quality of coal delivered to the various plants from the same car, there was unquestionably no such difference as is shown by the variation in these analyses, nor is it probable that the accuracy of these samples varies directly as the quantity of coal sampled. The fact that many of the plant samples did not exceed 100 pounds as originally taken is very strong evidence that errors of considerable magnitude were encountered through the smallness of these samples, and this is the point which I attempted to bring out in my original paper. I also referred to the sample taken from the cars as they were being unloaded under the supervision of Professor Lord as being by far more accurate than those taken at the different plants, while Mr. Weld's argument is to the contrary. It is certainly much more reasonable to assume that all of these samples were somewhat in error, and the lesser variation between the car samples and the average, as commented upon in my original paper and borne out by Mr. Weld's figures, where he states that the maximum error is only 1.16 per cent. However, if he had determined the errors from the individual plant samples as compared with the average obtained by his method, he would have found these errors to have been greater than they were by my original calculation. His average of the Iowa coal is 15.69, and the highest ash obtained from this was 20.70, an error of 5.01 per cent. The average obtained by my method was 16.60, and the error was only 4.10 per cent.

My criticism of the government work was not of the car samples, but of the plant samples, where only 100 pound original samples were taken. There is no question but that after this coal had been unloaded, crushed, conveyed, and delivered to the various plants, that the quantities delivered to the different plants were much more uniform in quality than is shown by the various analyses reported.

The application of the law of probability is recognized to apply only to errors which occur according to the law of chance, and does not apply to mistakes, personal or otherwise. The magnitude of the errors has little to do with the application of this law, even though Mr. Weld cites authorities to the contrary. However, he has not stated what kind of errors they referred to. They undoubtedly had in mind the application of the law of probability to the readings of instruments of precision, where any reading deviating far from the average is usually a mistake and not an error. Mr. Weld objects to applying this law to results of analyses which showed errors of 4.36 per cent. in ash in a coal which had an average of 11.50 per cent. ash, or which amounted to about 40 per cent. of the ash itself. Let us assume that a series of determinations were made in like manner from a sample of pure carbon which contained one piece of pure ash. Dividing this by the riffle sampler,

<sup>1</sup> *THIS JOURNAL*, 1, 161.

or any other method, it is obvious that the final quarter would or would not contain this one piece of ash. If this experiment were repeated several times, using different similar quantities with but one piece of ash, it is very evident that by the law of chance some would contain ash, others would be pure carbon. The variation upon the basis which Mr. Weld gives would be 100 per cent., yet it is perfectly evident that the law of probability would apply to this case equally as well as it does to the tossing of a coin or the dealing of poker hands. Upon Mr. Weld's basis of figuring the comparative magnitude of errors, the tossing of a coin embodies an error of 100 per cent., for it must either be heads or tails. There is unquestionably a misconception of the application of the law of probability in regard to the size of the errors; however, the law of probability applies to all cases where variations follow the law of chance, and are therefore classed as errors. The misconception of it not applying to large errors is due to a failure to distinguish between errors and mistakes.

In regard to the third question, as to the inadequacy of 1300 experiments, I would like to know of what value any one sample of any material must be, if the results of 1300 experiments are so worthless as Mr. Weld intimates. The question of extreme accuracy has little place in commercial work, and it is the errors of 3 to 5 per cent. in ash which are of ordinary occurrence that I attempted to point out and assist to remedy in commercial sampling.

In regard to the phrase "size-weight-per cent.," I cannot quite agree with Mr. Weld that this expression could be covered by the one word "size." However, this expression could have been conveyed by "percentage of the larger pieces of slate to the total weight of sample before being divided." As this factor was referred to several times in the paper, as well as in the tabulated matter, it was considered advisable to use the shorter expression so as not to encroach upon the readers' time by making a repetition of this sixteen-word expression.

In connection with the last paragraph of Mr. Weld's letter, I beg to refer to the last paragraph of my original paper, which is as follows: "Almost every one who has given any consideration to the sampling of coal or other similar material has said that a large sample should be taken and that it should be broken or crushed fine before the successive quarterings. How large, and how fine, have been left to the judgment of the individual taking the sample, and it is the object of this paper to answer these questions with some degree of accuracy. As this data is of preliminary nature, it is hoped that others will not only verify these results, but add to them, in order that the sampling of coal and other material may be reduced to a more scientific basis." Mr. Porter's paper has borne out this contention in showing the relation between "size-weight-per cent." and accuracy in sampling fertilizer.

Subsequent work along the line of my original paper has absolutely convinced me that mathematics can be properly and advantageously applied to the sampling of any material. The use of mathematics in this connection is of great assistance in determining when it is not necessary to take an exceedingly large sample, as well as to determine when a large sample should be taken.

E. G. BAILEY.

October 19, 1910.

#### REDUCTION OF TIN DROSS IN AN ELECTRIC FURNACE.<sup>1</sup>

Electrical heat was resorted to for the smelting of tin dross because of the fact that the heat could be internally applied to the slag, which is on the bottom of a shaft-type of furnace, thus enabling the dross to be thrown on top of the slag instead of being mixed with it as is done in the old-style furnace. The dross, being on top, comes in contact with the slag only at the

point of reduction. The liberated gases filter through the dross, while any tin oxide which is volatilized is condensed in the colder portion of the dross which, as I have said, is on top of the slag. The globules of tin produced in smelting pass downward through the slag and lose most of the impurities, so very little refining of the resultant product is necessary.

In operation, the top carbon, which is movable, is brought into contact with the lower carbon, which is stationary, and an arc formed. The slag is fed in and melted, and the carbon is raised until the desired amount of slag is added. The dross, mixed with the right percentage of carbon, is added, and the tin tapped from the bottom from time to time. The loss of tin has been kept as low as 0.25 per cent., and the average below 1 per cent. The amount of tin recovered varies largely on account of the varying percentages in the drosses treated. The average is about 2,500 pounds (1,100 kg.) per day.

The plant consists of two furnaces, connected in series, both being 20 inches (50 cm.) in diameter and 80 inches (200 cm.) high inside, two 50 kw. transformers and necessary electrical apparatus. In operation they consume about 44 kw. During the run it is desired to keep the amperage as near constant as possible, the voltage varying. At the start the voltage of each furnace is about 80, but toward the end, as the slag becomes less refractory, due to the combination of the iron and zinc of the dross and the slag, the voltage of each furnace will drop as low as 45-50. This and an analysis of the slag denotes the end of the operation, and the slag must be drawn out and new put in. This is done alternately with each furnace. The furnaces run continuously until time to be relined, which is about every three or four months.

R. S. WILE.

RIVERSIDE METAL REFINING CO.,  
CONNELLSVILLE, PA.

#### THE MODIFIED LAWALL METHOD FOR THE DETERMINATION OF SODIUM BENZOATE IN CATSUPS.

It became necessary in the course of work at this laboratory to gather some proof of the accuracy of the modified LaWall method for determining sodium benzoate in catsup. Accordingly, steps were taken to check this method with four well known brands of non-preserved catsups to which known quantities of sodium benzoate had been added. These catsups were first examined qualitatively for benzoic acid and sodium benzoate, and were found to be free from them. On account of the difficulty of obtaining sodium benzoate free from water, the preservative was weighed as benzoic acid, converted into sodium benzoate by dissolving in concentrated sodium hydroxide solution and in this condition added to 50 grams of catsup which had been previously weighed out. In order to do away with all possibility of the analyst being influenced by his knowledge of the amount of preservative added, the benzoic acid was weighed by another, and the writer was unaware of the amount added, except from his analyses, until after his results had been introduced as evidence in court.

The following table gives the per cent. of sodium benzoate added as calculated from the benzoic acid used, the per cent. found and the brands of catsup used in the experiment.

No.	Brand.	Per cent. added.	Per cent. found.
1	Columbia.....	0.118	0.118
2	Homelike.....	0.295	0.288
3	Shrewsbury.....	0.177	0.167
4	Beechnut.....	0.236	0.242

These results having proved conclusively the accuracy of the method when chemically pure preservatives were used, it next became necessary to determine its accuracy when commercial benzoate was employed. The writer in conjunction with a catsup manufacturer then made an experimental batch

<sup>1</sup> Read before the Chicago meeting of the American Electrochemical Society, October 13-15, 1910.

of catsup containing 0.1124 per cent. commercial sodium benzoate. This catsup when analyzed showed only 0.095 per cent. of the salt, and as this was obviously too low, the purity of the benzoate used was determined by dissolving 200 milligrams of the salt in 100 cc. of water, acidifying 50 cc. of this and extracting with four portions of chloroform, as is done in the actual method. This extracted solution was found by analysis to contain 86.4 milligrams of absolute sodium benzoate, and the commercial salt was therefore only 86.4 per cent. pure. When calculated on this basis of purity, the catsup showed by analysis 0.1099 per cent. sodium benzoate which is 0.0025 or 2.2 per cent. less than the amount added. This loss was undoubtedly due to part of the salt passing off with the steam in the process of boiling.

Still further investigation of the method was made by using the commercial benzoate and proceeding in exactly the same manner as when the chemically pure acid was used. In this experiment also the writer did not know the amount added until after his results were inserted in the court record.

The following table gives the amount of commercial salt added, the actual amount of salt found and the amount of commercial sodium benzoate, calculated as 86.4 per cent., pure, equivalent to the actual amount found.

No.	Brand.	Per cent. commercial salt added.	Per cent. chemically pure salt found.	Per cent. commercial salt found.
1	Columbia....	0.110	0.097	0.112
2	Columbia....	0.217	0.187	0.216

The method used was the modified LaWall and Bradshaw method, which is given as Method II on page 70, of the 1908 Proceedings of the A. O. A. C., and still further modified in this laboratory by the use of 50 grams of the sample instead of 200.

W. D. McABEE.

LABORATORY OF HYGIENE, STATE BOARD OF HEALTH,  
INDIANAPOLIS, INDIANA.

### BAKELITE.

With the incorporation of the General Bakelite Company, in New York, and the Bakelite Gesellschaft, m. b. H., in Berlin, an interesting invention enters upon its real commercial career.

We may point to the fact that in our issue of March, 1909, appeared for the first time the original paper which was read by Dr. Baekeland on this subject, before the American Chemical Society. This paper drew so much attention it was copied, translated and abstracted by many scientific and technical periodicals here and abroad.

More than a year has elapsed since, and considerable progress has been made on the practical side of the question. A brief up-to-date description of Bakelite is not out of place. Bakelite is a new substance, which, in its different forms, offers the advantages of hard rubber, Japanese lacquer, celluloid and in many respects excels the properties of these products.

It is not merely a mixture or a so-called "compound" like so many rubber, shellac, or other resinous compositions, but a well-defined chemical substance of specific properties; it thus adds an important member to the industry of plastics.

In the synthesis of Bakelite, we have a more recent instance of a laboratory reaction, which seems to run along lines parallel to those of the delicate physiological changes which occur in plant life; it has some relation to the subtle process which in the Japanese lacquer tree engenders the substance known under the name of Japanese lacquer. Up till now the latter has been a product of limited applications, and an article of luxury, on account of its excessive price, and scant supply. Henceforth a new material has become available which can be manufactured in practically limitless quantities and at a price which allows a wide range of uses.

The laboratory method is an improvement on nature's process, not only because the reaction is quicker and less expensive, but the resulting artificial product is decidedly more resisting to chemical and physical influences.

Dr. L. H. Baekeland, the inventor of this process, has a record of more than a quarter of a century of research in the field of pure and applied chemistry. To those outside of the chemical profession he is more particularly known through his inventive and industrial achievements in the industry of so-called gas-light photographic papers, of which Velox is the best known representative.

He presented the first general account of the synthesis of Bakelite and its industrial applications before the New York Section of the American Chemical Society on February 7, 1909, several years after he had started his investigations, on this subject, and after he had obtained due protection by filing the necessary patents here and abroad.

The word Bakelite was selected as a simpler trade-mark for the longer and less expedient chemical name oxybenzyl:methylenglycolanhydride.

For the layman it is somewhat startling that in the formation of Bakelite two strong smelling liquid substances (carboic acid and formaldehyde) should, under certain well-defined conditions, react chemically upon each other and solidify to a transparent amber-like solid substance entirely devoid of odor and taste.

The various uses of Bakelite will be better understood if we mention summarily some of its properties.

The final product, Bakelite C, is infusible and can resist temperatures of 572° F. (300° C.) or over. It is insoluble in all solvents, and can withstand strong chemicals, oil, hot water, steam, etc. All this in conjunction with its dielectric properties make it an excellent electrical insulator. It can be compounded with various filling materials and shaped or molded, with great accuracy to articles of unusual strength. It can be sawed, turned and polished.

It can be used to impregnate wood and other porous bodies, rendering them harder and more resisting to chemical and physical influences. Or it can be obtained as transparent as glass, or colored to suit special requirements.

It can be purchased at a reasonable price, the latter varying with its different qualities.

Although Bakelite is stronger and harder than celluloid or hard rubber, it lacks the unusual flexibility of both these plastics. Rods or plates made of it, or its compositions, are somewhat flexible, but considerably less so than celluloid or hard rubber. On the other hand, it withstands incomparably better, high temperatures and in general all chemical and physical influences, and has the further advantage of not being attacked by solvents nor by most chemicals. It does not emanate sulphur like hard rubber, nor nitrous products like celluloid, which have a very disturbing influence in some electrical applications. If heated in a flame, it does not suddenly catch fire like celluloid nor melt like rubber; it simply chars, then burns with difficulty.

During the act of hardening, which engenders the final product, there is a shrinkage of about two per cent. in diameter, or in length. This shrinkage can be lessened by the judicious incorporation of filling materials, and if the latter be used in large amounts, the decrease in volume can be reduced to such a point as to make it hardly perceptible. Its specific gravity is about 1.25.

The Bakelite process involves the utilization of three distinct and well-defined varieties of Bakelite, designated *Bakelite A*, *Bakelite B* and *Bakelite C*. *Bakelite C* is the final product, whereas *A* and *B* are the transition products, which enable us to mold or otherwise apply the material before its final condition.

*Bakelite A* is the initial raw material and exists in liquid, pasty or solid condition. Every variety of *A*, if heated at a



sufficiently high temperature, changes into *B*, then into *C*. All varieties of *A*, whether they be liquid, pasty or solid, are still soluble in alcohol or acetone or in caustic soda, and behave as true resins.

*Solid A* is characterized by the fact that it is solid at ordinary temperatures, but melts if moderate heat is applied and stronger application of heat makes it infusible and insoluble, by transforming it into *B* or *C*.

*Bakelite B* is an intermediate solid product. It is neither so hard nor strong as *C*, and may be easily mistaken for *Solid A*, but it is different from the latter on account of its insolubility. Furthermore, it is infusible, although the application of heat may temporarily soften it, without, however, bringing it into fusion. Solvents do not dissolve it, but some of them, like phenol or acetone, may soften it or swell it, without bringing it into solution. *B* is specially characterized by the fact that although it is infusible, it will soften under the action of heat and then will mold and weld together if pressed in a hot hydraulic press. The latter fact differentiates it clearly from *C*.

*Bakelite C* is the final product, resulting from the application of heat to *A* or *B*, and may be considered as a chemical polymer of *B* resulting from a multiple molecular grouping. It is no longer a resin, because it lacks all the chemical characteristics of a resin, although physically it may resemble amber. In pure form, and if made from the first member of the phenol group, its chemical formula is represented by  $C_{10}H_8O_7$ .

Although the preparatory work connected with the industrial side of the process has been going on with strenuous application since 1907, it was thought advisable not to jeopardize everything by a too hasty, broadcast introduction, before each industrial use had been studied for a sufficiently long time, on a practical commercial scale. This conservative way of proceeding is not always followed by those who are not sufficiently aware of the enormous distance that exists between a laboratory conception and the practical utilization thereof.

In the meantime, Bakelite has been used continuously during the last two years, especially for electrical purposes, while undergoing the test of time and the critical observations of everyday practice under the eyes of specialists. This work has been conducted on a sufficiently large scale to remove all doubts as to the practical side of the question. Thus Bakelite is no longer a laboratory experiment but a product well tried in several industries.

Bakelite technical insulators, as well as pump valves, and other molded goods are now obtainable from several licensees of the General Bakelite Company, and some electrical manufacturers have begun the practical impregnation of coils, dynamos, motors, etc.

The General Bakelite Company will limit more specially their attention to the chemical side of the process manufacturing the raw materials, just far enough that the users thereof can limit their attention to the mechanical side of the problem.

A factory plant is being equipped now at Perth Amboy, N. J., but in the meantime the manufacturing is being carried on in Yonkers. In our November number, 1910, page 478, we have published a list of the United States patents, thus far issued.

An information book on practical uses of Bakelite can be obtained by applying to the General Bakelite Company, 100 William Street, New York, N. Y.

#### THE USE OF IMMISCIBLE SOLVENTS.

There are several methods in use by food chemists, some of them recognized as official by the A. O. A. C., which involve the use of immiscible solvents, as for instance, the modified Hess and Prescott method for determining vanillin in vanilla extracts, and Bigelow's modification of the LaWall and Brad-

shaw method for the estimation of benzoic acid in food products. It is a well-known fact that ether and chloroform which contain water or are in contact with water will take up appreciable amounts of inorganic salts. This has been found to constitute a continual source of error in such determinations.

In the Hess and Prescott method for vanillin the extraction is made with ether from a solution which contains more than 2 per cent. of ammonium chloride. With utmost care in the separation, the residue from the ether solution will still give a strong test for chlorides. Similarly in the method for benzoic acid, where extraction is made from a saturated salt solution with chloroform, considerable quantities of salt will invariably be found in the residue.

The writer has found it necessary in all cases to take up the residue with a little anhydrous ether, and again evaporate, to secure anything like concordant results.

ROE E. REMINGTON.

AGRICULTURAL COLLEGE, NORTH DAKOTA.

#### MAKING SAMPLE ALLOYS.

Those of us who are teaching qualitative analysis frequently find it difficult to obtain any number of different samples of industrial products. This has been, in my case, especially true of alloys of the more modern types such as ferro-chrome, nickel, steel, etc., which it is very desirable for the student to have practice on.

In case of these alloys it has been possible to make them with very little consumption of time. Black thermite (iron oxide and finely ground metallic aluminium) can be readily obtained. This, when placed in a common assay crucible, mixed with the element or elements with which it is wished to alloy the iron, and ignited in the usual way by means of a fuse of magnesium ribbon and an igniting mixture of finely powdered aluminium and sodium peroxide, generates sufficient heat to form a homogeneous button of the alloy desired, in the bottom of the crucible.

If alloys, which do not contain iron, are desired, equally good results can be obtained by making mixtures of the oxides of the required metals in the proper proportions with metallic aluminium and igniting as before. I have found alloys made in this way very satisfactory for qualitative analysis and that it is possible to make them with a very small consumption of time.

R. C. BENNER.

UNIVERSITY OF ARIZONA, TUCSON.

#### LABORATORY METHODS FOR ORGANIC NITROGEN AVAILABILITY.

##### MODIFIED ALKALINE PERMANGANATE METHOD.

As used by C. H. JONES, Vermont Station.

1. *Total Organic Nitrogen Basis*.—Weigh an amount of material equivalent to 50 milligrams organic nitrogen into a 600 cc. Kjeldahl distillation flask. Add 20 cc. of water and 100 cc. of alkaline permanganate solution (25 grams pure  $KMnO_4$  and 150 grams  $NaOH$  separately dissolved in water, the solutions cooled, mixed, and made to bulk of one liter). Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly (below distillation point) for 30 minutes. Gradually increase temperature and boil until 95 cc. of distillate are obtained; titrate as usual. Make a correction for any ammonia contained in the sample. During the digestion an occasional gentle rotation is desirable, and if the material shows a tendency to adhere to the sides of the flask during the distillation, the same procedure is advised. The per cent. of nitrogen obtained on the above 5 per cent. basis  $\times 20$  = per cent. availability.

2. *Water-insoluble Nitrogen Basis*.—Weigh an amount of

material equivalent to 50 milligrams of *water-insoluble organic nitrogen*<sup>1</sup> on a filter. Wash with successive portions of water until the filtrate amounts to about 250 cc. Dry the residue at a temperature not exceeding 80° C. and transfer same *from the filter* into a 600 cc. Kjeldahl distillation flask. Add 20 cc. of water and 100 cc. of alkaline permanganate solution and proceed as under 1. No correction is necessary for ammonia.

#### NEUTRAL PERMANGANATE METHOD.

As used by J. P. STREET, Connecticut Station.

Weigh a quantity of the fertilizer, equivalent to 45 mg. of *water-insoluble organic nitrogen*<sup>1</sup> on a moistened 11 cm. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, and add 100 cc. of 2 per cent. permanganate solution. Digest in a steam or hot-water bath for thirty minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of ten minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correction for the nitrogen of the filter.

#### CHEMICAL INDUSTRY AT BRUSSELS' EXPOSITION.

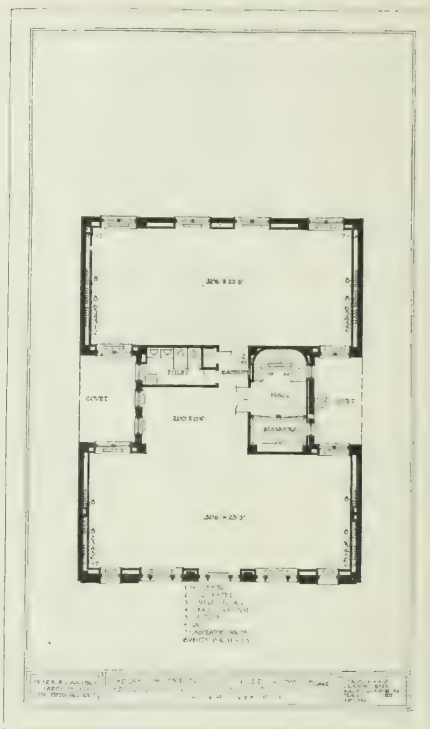
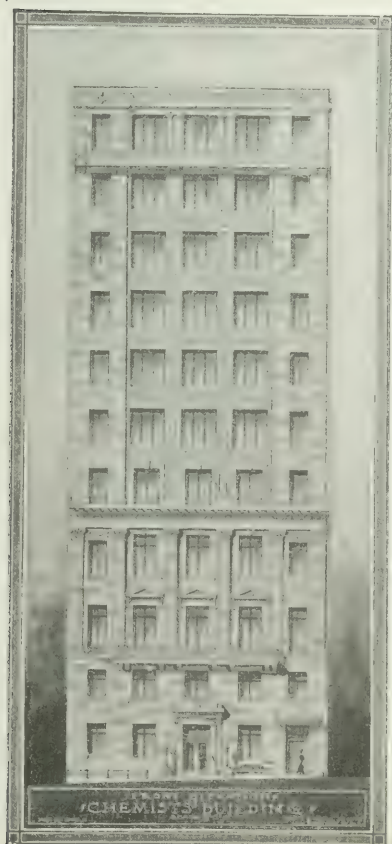
Chemical Industry at the Brussels' World Exposition. H. Grossman, *Chem. Ind.*, 33, 569-78.—The author discusses mostly the status of chem. ind. in the different countries represented by exhibits. *Germany*.—Ger. manufacturers showed novelties in chlorate and  $\text{NH}_4\text{NO}_3$  (safety) explosives. Dorfite and alldorfite contain  $\text{NH}_4\text{NO}_3$  and trinitrotoluene and are allowed rail conveyance. Trinitrotoluene in the pure state finds use as "Trinol" for filling shells, and rendered plastic by the addition of liquid dinitrotoluene and  $\text{Pb}(\text{NO}_3)_2$  finds application as "Triplastit." The perfumery and toilet soap ind. of Ger. is growing in spite of the sharp foreign competition and the domestic preference for French products. In 1907 the No. of workers in this ind. was 5000, and the imports amtd. to \$2,856,000 in 1909, being \$357,000 less than in 1908. A Munich firm exhibited aluminized balloon and aeroplane materials, the advantages claimed being the strong reflection of heat rays and the slight adhesion of atmospheric ppts. At the present time in Ger. there are 70 electric steel furnaces in action which produce 20 million kg. steel yearly. Concerning gas production, within 4 yrs. have been built or are building 507 Dessau ovens with 5414 retorts and with a daily output of about 2.2 million cu. m. gas. A Berlin firm shows "Silvalin," a textile fabric made from wood fiber, esp. adapted for workmen's clothing because of its price (less than cotton). *England*.—The Le-Blanc soda process is used by the United "Alcali" Co. and the author states that it is still in operation in 3 factories in Ger. The International Salt Co. employing the "Teer" process (which consists in removing the impurities of rock salt by fusing in a special app.) obtains 15,000 kg. pure table salt with a consumption of 1,000 kg. coal. Recently a part of the Cl obt. in the electrolysis of alk. chlorides has been converted into compds. of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  used as solvents for fats. The Mond-Nickel Co. by the Mond process uses the electric current to produce an almost c. p. Ni from Sudbury ores. Sundry imports for 1907 follow expressed in millions of kg.: tallow, 105.0; palm oil, 60.7; cocoanut oil, 23.8; castor oil, 6.1; palmmut oil, 14.7; corn oil, 14.4; olive oil, 12.3. In 1908 were imported 617

<sup>1</sup> Determined by washing one gram of the material on a 11 cm. filter with water at room temperature, to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

million kg. cottonseed as against 750 in 1907. From this was extracted 110 million kg. oil. Since the first of 1909 no less than 400 million kg. of soy beans have been imptd. from Japan, the bean serving not only for its oil but the albuminous resid. as food. The candle ind. consumes about 40 million kg. paraffin, half being from Scotland and half from Amer. The soap exports of Eng. amtd. in 1907 to \$7,085,880. In the past yr. in Scotland nearly 3 billion kg. bituminous shale gave a yield of 309 million l. of raw oil which upon refining gave the folwng. amts. of oils: burning, 100 million l.; power, 18 million l.; gas, 40 million kg.; and 25 million kg. paraffin, with a by-production of 60 million kg.  $(\text{NH}_4)_2\text{SO}_4$ . *France*.—The discovery of large deposits of an excellent calcareous Fe-ore in the basin of Briey in French Lorraine is noteworthy. The output of this ore has risen from nothing a few yrs. ago to 1.68 billion kg. in 1909 and now constitutes nearly 60 per cent. of the entire Fr. output. *Belgium*.—Here the chem. ind. is concerned mostly with the working up of sol. products, esp. minerals. The rich coal fields in the south have caused the growth of a considerable tar and  $(\text{NH}_4)_2\text{SO}_4$  production. The latter is obt. by the direct process after a precooling of the hot retort gases. This salt is the only fertilizer used in Belg. Most of the tar products are exported.  $\text{H}_2\text{SO}_4$  is obt. in great amts. as a by-product in the roasting of Zn blende and is partly worked up into superphosphate and  $\text{Na}_2\text{SO}_4$  and partly exported to Ger. In Belg. glass manuf., the chief consumer of  $\text{Na}_2\text{SO}_4$  is of extreme importance. Nine companies belong to the international trust. The central office of Solvay & Co. which controls the soda market of the world is situated in Brussels. The original factory in Couillet employs 430 men. In France this syndicate has 2 factories employing 2100 and 450 hands resp. Spain is supplied by a factory which, inclusive of its salt works and coal mine, employs 600 men. In Eng. the Solvay Co. is heavily interested in a Co. which possesses 5 factories and has 4000 workmen. In Ger. it is concerned with a Co. that in 6 factories employ about 5,000 men and uses over 21,000 H. P. Russia has 3 Solvay factories and Austro-Hungary 5. The S. Co. possesses the European patents of Castner and Kellner and besides mfg. NaOH itself it also has licensed numerous concerns on the continent. In its Belg. factories it has introd. the 8-hr. day with no reduction in pay from the 9 1/2-hr. day. The 8-hr. day is also operative in the English S. Co. The factories in Syracuse, N. Y., and Detroit, Mich., are the largest in the world. The highly developed textile ind. of Belg. is responsible for the great soda consumption. A very successful artif. silk factory is in operation. The stearin candle soap, gelatine and glue, and pharm. industries are noteworthy. For a report on the Belg. explosive and match ind. cf. *C. A.*, 4, 2572. *Italy*.—The extraction of Fe ore has not kept pace with the growth of the Fe and steel ind. Considerable steel is made in the electric furnace. The explosive, cheddite, is mfd. in Italy, France (the home factory), Switzerland, Greece, Tonkin, Eng., Reunion Isle, Belg., Uruguay and Ger. The tanning materials, soap, perfume and pharm. inds. of Italy are highly developed. *Canada*.—In 1907 C. stood in first place as a producer of Ni and asbestos (and latterly Co), in 3d for Cr ore, in 4th for Ag ore, in 7th for Cu, in 8th for Au, and in 10th for coal. Cf. the excellent publication of the *Bureau of Mines*, "Geol. Sketches and Mineral Resources of C.," by G. A. Young, Ottawa, 1910; also cf. *Chem. Ind.*, 33, 402. *Brazil*.—In 1907 the export of Mn ores amtd. to 237 million kg. valued at \$4,500,000. That of monazite sand amtd. to 4,437,000 kg. as \$890,000. Coal and Fe production is in its infancy due to lack of railroad facilities. There are large deposits of these minerals of good quality, the latter showing a high Fe content. The State Mines Geraes in 1909 produced nearly 4,000 kg. Au. Similarly situated as Brazil in respect to their human material and railroad conditions are Uruguay, Nicaragua, Guatemala etc., where the smelting of ores and the winning of valuable drugs have as yet made little

advance although the possibilities exist. *French Colonies.*—A table shows the phosphate output of Tunis and Algiers, its value and the amts. exported for the yrs. 1899–1909 incl. In 1909 the value was \$5,257,513 and the Algerian expt. 333,400,000 kg. The mineral averages 58–68 per cent. Ca phosphate. Despite the crisis in the phosph. market the output of Tunis of 1909 was but little less than that of 1908, and an increase is to be expected next yr. In 1909 there were 44 mining concessions which exported Zn, Pb, Cu, and esp. Fe ore to the value of \$2,211,780. From Algiers were exptd. the folwng. amts. of ores expressed in millions of kg., the output being for 1905–09 incl.: Fe, about 800; Cu, 4.5; Pb, 19; Zn, 70; Sb (since 1907), 1.5. Sea salt is extr. in Tunis to the amt. of 150 million kg. yearly which is exported. Alpha grass used in the manuf. of paper is a valuable export. New Caledonia specializes in Ni ore production, the output being worked up in France by "Le Nickel." It also produces much Cr. *Congo State.*—This next to Brazil yields the greatest amt. of rubber, 4,650,000 kg. valued at \$8,488,140 being the 1907 output. Of palm oil, palm nuts and copal there were exported in 1908 the folwng. resp. amts. expressed in millions of kg.: 2.1 at \$231,600; 5.6 at \$335,820; and 1.66 at \$345,470. Inland are extended deposits of high per cent. Cu, Pb and Zn.

L. RAY FERGUSON.



#### CHEMISTS' BUILDING.

The Chemists' Building Company of New York City, organized to promote the interests of Chemical Science and Industry in America, has erected a ten-story fire-proof building, on a lot 56 ft. wide and 100 ft. deep, at 50–54 East 41st Street, New York City.

The lower half of the building is leased to the Chemists' Club, and contains all the appurtenances of a social club, together with a large auditorium for scientific meetings and ample space for a complete chemical library and museum.

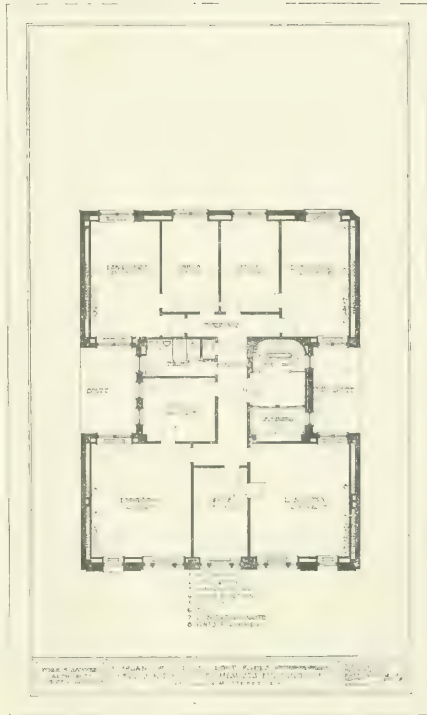
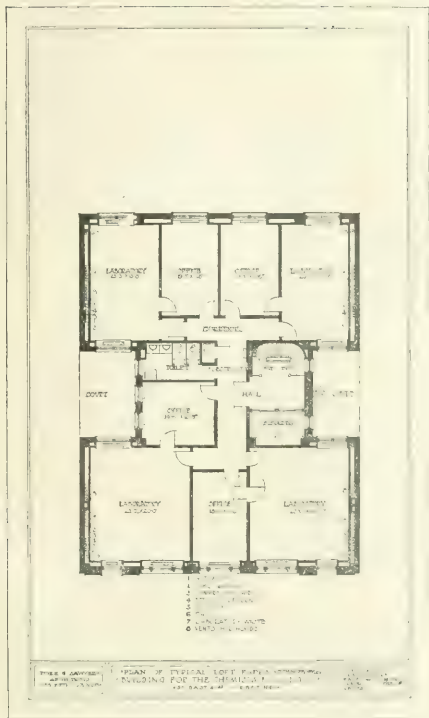
The five upper stories have been specially constructed for laboratory purposes, and can be rented either as entire floors, or in suitable sub-divisions, to analytical, commercial or research chemists, physicists, electrochemists, bacteriologists, etc.; but not as manufacturing laboratories.

They are provided with ventilating flues, water, gas and electric mains, steam and compressed air lines, in suitable locations; but the tenants are expected to make their own connections and provide their own fixtures.

Rental will include free janitor and elevator service, heat and electricity for lighting purposes, and the Company will construct proper partition walls for the subdivision of the laboratories, according to the tenants' wishes. It is intended to charge low rentals and in many ways facilitates the prosecution of scientific and industrial research.

*Location.*—Close to the Grand Central Station and the 42nd Street Express Station of the Subway, as well as to the prospective termini of the "Steinway" and "McAdoo" terminal systems; a few minutes' walk from the New York Public Library, Engineering Society's Building and Academy of Medicine.





*Advantages within the Building.*—Excellent light and ventilation; construction equal to that of university laboratories; command of a complete chemical library; opportunities for social and scientific intercourse; the natural meeting-place of out-of-town chemists and manufacturers, for whom the Club provides excellent apartments; possibility for reduction of laboratory expenses through coöperative installation of expensive apparatus.

The value of this neighborhood for such purposes has been further indicated by the erection of a large physicians' and dentists' building alongside, and the attention of physicians and pathologists is called to the advantages which the Chemists' Building laboratories could afford them for their own researches.

Until February 1st, communications should be addressed to Dr. Morris Loeb, President, 106 West 55th Street. After that date, his office will be in the Building, 50 East 41st Street.

## BOOK REVIEWS AND NOTICES.

**A Text-Book of Botany and Pharmacognosy.** Intended for the Use of Students of Pharmacy, as a Reference Book for Pharmacists, and as a Hand-Book for Food and Drug Analysts. By HENRY KRAEMER, Ph.D., Ph.B. 888 pages, illustrated, 4th edition, revised and enlarged. Philadelphia: J. B. Lippincott and Co. 1910. Price, \$5.00 net.

This book is well known in schools of pharmacy where for some years it has been recognized as a standard work, while the nature of the book makes it naturally of somewhat limited interest to chemists; it possesses certain features which deserve more than a passing notice in this place.

The work is divided into four parts: Part I, in five chapters, covers the general subject of botany as related to medicinal plants; Part II is concerned with a study of crude drugs as derived from these plants, while Parts III and IV, which are much shorter than the others, deal with reagents and technique and methods of microchemical analysis.

In Part II there is a great deal of information on this subject of plant constituents which will be found very useful to any one interested in the chemistry of drugs and drug analysis. In

view of the many questions coming up under the Food and Drugs Act the data found in this section of the book should be appreciated. Professor Kraemer has devoted much study to the microchemistry of drugs and methods of identification. In Part IV the newer developments in this field are discussed; the opinion is expressed that the petrographical microscope will prove as useful in the study of the crystalline constituents of drugs as it has in other directions. The value of this general method is illustrated by the details of a number of practical examinations on well-known crystals which occur in certain drugs. The method of securing the crystals is explained and enough is presented to make the general plan of identification helpful and suggestive to the drug analyst. J. H. LONG.

**Handbuch der Chemie und Technologie der Oele und Fette.** In four volumes, Vol. 3, first part. By L. UBBELOHDE AND F. GOLDSCHMIDT and a large number of collaborators. Large 8vo. pp. xx + 380. Leipzig: S. Hirzel, 1910. Price, paper, 12 Marks.

The previous volumes of this large work on the oils and fats have been noticed in these columns. The present volume considers the chemistry, analysis, and technology of the fatty

acids, glycerin, and Turkey-red oil. The first part is on the subject of the splitting of fats and the production of raw glycerine, and takes up in detail the autoclave, Twitchell fermentative and Kriebetz processes. Finally the technology of crude glycerine is treated. The second part is devoted to the distillation refining, application and analysis of glycerine. The third part covers the stearine industry including candle-making and the fourth part Turkey-red oil. For the most part the work treats of German practice more fully than that of other countries. Recent American practice is neglected or treated only partially. The historical introductions to most of the subjects are good although brief. The illustrations are abundant and excellent. It is a book to be recommended.

**Chemisch-Technische Untersuchungsmethoden.** By DR. GEORG LUNGE AND DR. ERNST BERL AND OTHERS. Vol. 2, 6th edition. Large 8vo. pp. xvi + 869. Berlin: Julius Springer, 1910. Price, paper, 20 Marks. Bound, 22.50 Marks.

This is the second volume of Dr. Lunge's well-known book on technical analysis which has reached the sixth edition. It is the only work which covers the whole field of chemical technical analysis and, considering the great number of subjects to be treated and the diversity of chemical methods, covers it remarkably well. The present volume discusses the following subjects: Cyanides, clays, ceramics, glass, lime, Portland cement, plaster, water, sewage, soil, air, iron, silver, gold, platinum, mercury, copper, lead, bismuth, tin, arsenic, antimony, zinc, cadmium, nickel, cobalt, manganese, chromium, tungsten, uranium, vanadium, molybdenum, aluminium, thorium, tantalum, metallic salts, calcium carbide and acetylene. The work is well illustrated for the most part with small cuts in the text. It is needless to say that it is one of the indispensable books in the analyst's library.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### AMERICAN CHEMICAL SOCIETY.

Winter Meeting. Minneapolis.

The Winter meeting of the American Chemical Society will be held in Minneapolis, December 28-31, 1910. The American Association for the Advancement of Science meets in Minneapolis at the same time. The local committee is hard at work under the leadership of Dr. G. B. Frankforter, and the meeting will probably be one of the largest and most enthusiastic ever held. The officers of the various Divisions and Sections are shown in the following list:

#### Divisions.

*Agricultural and Food Chemists.*—Chairman, H. E. Barnard, Board of Health, Indianapolis, Ind. Secretary, B. C. Curry, Durham, N. H.

*Fertilizer Chemists.*—Chairman, F. B. Carpenter, Richmond, Va. Secretary, J. E. Breckenridge, Carteret, N. J.

*Industrial Chemists and Chemical Engineers.*—Chairman, A. D. Little, 93 Broad St., Boston, Mass. Secretary, F. E. Gallagher, 93 Broad St., Boston, Mass.

*Organic Chemists.*—Chairman, E. C. Franklin, Stanford University, Cal. Secretary, Ralph H. McKee, Orono, Maine.

*Pharmaceutical Chemists.*—Chairman, A. B. Stevens, University of Michigan, Ann Arbor, Mich. Secretary, B. L. Murray, Merck & Co., New York City.

*Physical and Inorganic Chemists.*—Chairman, E. C. Franklin, Stanford University, Cal. Secretary, S. L. Bigelow, Ann Arbor, Mich.

#### Sections.

*Biological Chemists.*—Chairman, to be announced.

*Chemical Education.*—Chairman, H. P. Talbot, Mass. Inst.

Tech., Boston, Mass. Secretary, James F. Norris, Simmons College, Boston, Mass.

*Chemistry of India Rubber.*—Chairman, C. C. Goodrich, 25 Broad St., New York City. Secretary, F. J. Maywald, 1028 Seventy-second St., Brooklyn, N. Y.

Reports of the sessions of the Division of Industrial Chemists and Chemical Engineers, the Division of Fertilizer Chemists, the Division of Pharmaceutical Chemists, and the Division of Agricultural and Food Chemists will be published in the January and February numbers of THIS JOURNAL, as usual.

### THIRD ANNUAL MEETING OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

New York City, December 7 to 10, 1910.

#### PROGRAM.

WEDNESDAY, DECEMBER 7, 1910.

9.30 A.M.—Meeting at Hotel Astor. Address of Welcome, Hon. John Purroy Mitchell, President of the Board of Aldermen, City of New York.

*Business Session.*—Canvass of ballots for officers. Reports of officers and council. Report of committees.

11 A.M.—Reading of Papers: "Report of the Committee on Chemical Engineering Education," F. W. Frerichs. "The Development of the Chemist as an Engineer," Dr. Fred W. Atkinson, President of the Brooklyn Polytechnic Institute. "The Training of Chemical Engineers which Meets the Requirements of Manufacturers," Prof. M. C. Whitaker, Columbia Univ.

Discussion: The Fitzgibbons Boiler, Jerome Alexander.

12.30 P.M.—Luncheon.

1.30 P.M.—Excursions: Marx and Rawolle Glycerine Refinery, Brooklyn, N. Y. Wood's Multiple Effect Stills are in operation at this plant.

8.00 P.M.—Meeting at Columbia University. Address of Welcome, Prof. M. T. Bogert. Reply, The President of the Institute. "Manufacture of Hydrated Lime," Richard K. Meade. Address of Retiring President, Chas. F. McKenna, "The Evolution of Portland Cement Processes." Discussion.

THURSDAY, DECEMBER 8, 1910.

9.30 A.M.—Excursions: Chamber Acid Plant of the Standard Oil Company at Bayonne, N. J. This is a very large modern plant, the concentration apparatus being especially interesting. Through the courtesy of the Standard Oil Company the members of the Institute and their guests will be conveyed by a steam lighter to Constable Hook and return. The boat will leave Pier 4, North River, at 9.30 A.M. Luncheon at Hugot's Restaurant, New Brighton, S. I., 75 cents.

2.00 P.M.—Visit to the Borough of Richmond Garbage Destructor at the invitation of the Heenan Destructor Co.

7.00 P.M.—Subscription dinner at Hotel Astor, \$3.00.

FRIDAY, DECEMBER 9, 1910.

9.30 A.M.—Meeting at Hotel Astor. Installation of Officers. Business session.

10.30 A.M.—Reading of Papers: "Manufacture of Lignite Briquettes," Henry S. Renaud. "Bleaching Oils with Fuller's Earth," David Wesson. "Action of Fruit Juices on Metallic Containers," Edward Gudeman.

1.00 P.M.—Excursions: Visit to Candle House of the Pratt Works of the Standard Oil Company at Blissville, L. I.

3.30 P.M.—Visit to Grease Works of the same Company at Blissville, L. I.

8.15 P.M.—Joint meeting with the New York Section of the

American Chemical Society, at Chemists' Club, 108 West 55th St., Prof. Charles Baskerville, Chairman of the Section, presiding. Reading of Papers: "The Principles of Sewage Disposal," Geo. C. Whipple. "Sewage Disposal in Europe," Rudolph Herring. "Sewage Disposal in New York and Vicinity," Dr. Geo. A. Soper. "Sanitary Conditions in Their Relation to Water Supplies in the Vicinity of New York," Nicholas S. Hill, Jr. "The Unsolved Problems of Sewage Disposal," Prof. Chas. E. A. Winslow. Discussion.

SATURDAY, DECEMBER 10, 1910.

Excursions: Inspection of Chemical Museum and Laboratories of Columbia Univ. Inspection of Chemical Building and Laboratories of the College of the City of New York.

Headquarters at Hotel Astor, Times Square. Rates at this hotel, European plan:

Room without bath, one person.....	\$2.50 and up.
Room without bath, two persons.....	\$3.50 and up.
Room with bath, one person.....	\$3.50 and up.
Room with bath, two persons.....	\$4.50 and up.

# COMMITTEE OF REVISION OF THE PHARMACOPOEIA OF THE UNITED STATES OF AMERICA.

Sub-Committees, with Chairmen.

No. 1.—Scope (Admissions and Deletions). S. Salis Cohen, M.D., Philadelphia.

No. 2.—Therapeutics and Pharmacodynamics. Torald Sollmann, M. D., Cleveland, O.

No. 3.—Biologic Products and Diagnostic Tests. J. F. Anderson, M.D., Washington, D. C.

No. 4.—Botany and Pharmacognosy. Henry Kraemer, Ph.D., Philadelphia.

No. 5.—General and Inorganic Chemistry. Chas. H. LaWall, Philadelphia.

No. 6.—Organic Chemistry. Geo. D. Rosengarten, Ph.D., Philadelphia.

No. 7.—Proximate Assays. A. B. Stevens, Ph.D., Ann Arbor, Mich.

No. 8.—Volatile Oils. H. W. Wiley, Ph.D., Washington.

No. 9.—Fluid and Solid Extracts, Tinctures. G. M. Beringer, Philadelphia.

No. 10.—Aromatic Waters, Spirits, Liquors. C. Lewis Diehl, Louisville, Ky.

No. 11.—Syrups and Elixirs. W. C. Alpers, Sc.D., New York.

No. 12.—Cerates and Ointments. Otto Raubenheimer, Brooklyn.

No. 13.—Miscellaneous Galenicals. C. S. N. Hallberg, M.D., Chicago.

No. 14.—Tables, Weights, Measures. A. B. Lyons, M.D., Detroit.

No. 15.—Nomenclature. Chas. Caspari, Baltimore.

# ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

Twenty-seventh Annual Convention. Washington, November 10-12, 1910.

The program of this meeting has already been published in these columns (see September number). The officers elected for 1910-1911 are:

President, F. W. Woll, Madison, Wisconsin.

Vice-Presidents, H. J. Patterson, Maryland.

Secretary, H. W. Wiley, Washington, D. C.

Additional Members of the Executive Committee. H. C. Lythgoe, Massachusetts; P. F. Trowbridge, Missouri.

The meeting opened on Thursday morning, November 10th, at the Raleigh, with President W. A. Withers, of Raleigh, N. C., in the chair.

No report was offered by the referee on phosphoric acid, W. F. Hand, of Agricultural College, Mississippi, but a paper on the Wagner method was read by W. L. Whitehouse, of the Coe-Mortimer Company, New York City. Mr. Haskins, of the Massachusetts Station, stated that he would like to see this method adopted by the Association, as he considered it the only one satisfactory for the determination of phosphoric acid in basic slag, and that the state officials were obliged to handle many different brands of this material. No action was taken.

C. H. Jones, of the Vermont Station, referee on nitrogen, presented no recommendation on nitrogen, but gave a short paper dealing with the availability of organic nitrogen by laboratory methods. This paper was presented merely as a suggestion for further work. Fig. 1 shows plotted results.

The report on potash was submitted by E. L. Baker, of the Geneva (New York) Station, and consisted in a continuation of the study of the Drushel's Volumetric Cobalti-Nitrite method in comparison with the official. In addition a gravimetric

TABLE I.—COMPARATIVE RESULTS OF OFFICIAL, VOLUMETRIC AND GRAVIMETRIC COBALTI-NITRITE METHODS.

	Sample No. 1.			Sample No. 2.			Sample No. 3.			No. 3.
	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Modified method.
B. E. Curry, Durham, N. H.	Ave. 50.70	50.11	51.19	12.45	12.16	12.48	4.64	4.48	5.37	4.71
P. L. McCreary and P. L. Hibbard	Ave. 51.68	47.22	50.61	12.73	12.21	12.44	4.68	4.07	4.96	4.48
Cornelius Beatty, College Park, Md.	Ave. 53.25 <sup>1</sup>	51.43	52.22	12.67	12.65	12.87	4.92 <sup>1</sup>	4.34	5.15	5.07 <sup>1</sup>
W. W. Murray, Baltimore, Md.	Ave. 52.12	51.53	52.49	12.60	12.18	12.41	4.63	4.54	4.94	4.70
I. R. Rothrock and A. C. Johnson	Ave. 51.71	51.75	51.80	12.51	12.54	12.55	4.74	.....	.....	4.66
O. M. Shedd, Lexington, Ky.	Ave. 52.01	51.60	.....	12.82	12.60	.....	4.66	4.66	.....	.....
R. C. Wiley, Manhattan, Kan.	Ave. 51.99	47.56 <sup>1</sup>	47.14	12.82	10.85 <sup>1</sup>	11.94	4.89	4.69	6.31	4.85
L. F. Whipple, Kingston, R. I.	Ave. 51.05	50.86	51.98	12.60	13.01	12.95	4.76	4.52	6.79	.....
R. M. Pinckney, Bozeman, Mont.	Ave. 52.02	51.56	54.35	13.12	12.41	13.23	4.56	4.43	6.48	.....
E. L. Baker, Geneva, N. Y.	Ave. 51.96	52.09	51.18	12.86	12.93	12.81	4.62	4.65	4.83	4.81
William Rodes, Lexington, Ky.	Ave. 52.00	.....	.....	12.72	.....	.....	4.72	.....	.....	4.86
Otto McCreary, Geneva, N. Y.	Ave. 51.99	53.01	53.80	12.76	12.76	12.90	4.65	4.71	4.66	4.86
H. H. Hill, Blacksburg, Va.	Ave. 51.93	51.80	51.95	13.00	12.84	13.11	4.67	4.50	4.56	4.80
M. P. Sweeney, Geneva, N. Y. <sup>2</sup>	Ave. 51.89	51.42	51.95	12.63	12.97	12.93	4.70	4.62	4.66	4.89
C. C. Hedges and F. E. Rice <sup>3</sup>	Ave. 52.02	51.04	51.99	12.83	12.54	12.86	4.65	4.38	4.76	4.78
J. C. Jurrjens, Madison, Wis. <sup>2</sup>	Ave. 50.85	50.01	50.41	12.27	12.31	12.61	4.77	4.69	7.77	5.28
L. E. Morgan, Columbia, Mo. <sup>2</sup>	Ave. 52.34	53.78	54.85	13.73	13.20	13.18	4.98	4.86	5.38	.....
General average.....	51.77	50.92	50.72	12.73	12.61	12.72	4.69	4.53	5.33	4.81

<sup>1</sup> Omitted from average.

<sup>2</sup> Received too late to be included in average.

<sup>3</sup> Precipitated at a concentration of 5 cc. and used 15 cc. of reagent.



method using the cobalti-nitrite reagent as a precipitant, and the test of the modification of the official method by making up the potash solution as described by Breckenridge<sup>1</sup> were included in the work. The three samples used were commercial muriate, kainit, and a complete mixed fertilizer. The comparative results obtained are given in Table I. The conclusions reached were as follows: "By the volumetric method as outlined the majority of the analysts have obtained satisfactory results. Probably the variation occurring in the muriate

Mr. J. A. Bizzell, of the Ithaca (New York) Station, associate referee on available potash, stated that "With our present knowledge of soils we are not justified in attempting to devise laboratory methods for the determination of available potash. The loss of water-soluble potash, when potash salts are mixed with acid phosphate, should be further investigated."

The next report presented was that on soils by J. G. Lipman, of the New Jersey Station. In the absence of Dr. Lipman the report was read by Mr. Cathcart. The coöperative work con-

TABLE II.—INORGANIC PLANT CONSTITUENTS.

Analyst.	No. of determinations.	Sulphur in plants—Peroxide method.					
		Graham flour, per cent. SO <sub>2</sub> .			Linseed meal, per cent. SO <sub>2</sub> .		
		Min.	Max.	Ave.	Min.	Max.	Ave.
W. H. Ross, Tucson, Ariz.....	3	0.357	0.466	0.413	0.748	0.857	0.797
Firman Thompson, Newark, Dela.....	3	0.339	0.377	0.352	0.832	0.913	0.866
W. H. Peterson, Madison Wis.....	3	0.442	0.474	0.457	0.911	0.952	0.937
R. O. Baird, Stillwater, Okla.....	5	0.350	0.408	0.377			
	6				0.823	0.899	0.867
O. M. Shedd, Lexington, Ky.....	5	0.364	0.394	0.379			
	4				0.820	0.833	0.826
W. H. McIntire, State College, Pa.....	2	0.367	0.383	0.375	0.824	0.875	0.850
F. W. Sherwood, W. Raleigh, N. C.....	4	0.285	0.352	0.321	0.692	0.731	0.708
A. T. Charron, Ottawa, Canada.....	2	0.463	0.470	0.467	0.922	0.926	0.924
J. P. Aumer, Urbana, Ill.....	3	3.340	0.353	0.346			
	2				0.833	0.853	0.843
O. B. Winter, E. Lansing, Mich.....	4	0.353	0.391	0.373	0.858	0.947	0.887
R. M. Pinckney, Bozeman, Mont.....	4	0.306	0.412	0.377			
	3				0.699	0.830	0.773
G. E. Boltz, Wooster, O.....	1		0.394			0.874	

Average of 39 determinations on the graham flour shows 0.381 per cent.

Average of 37 determinations on the linseed meal shows 0.841 per cent.

may be avoided by increasing the size of the aliquot. It seems safe to predict that with slight modification an accurate optional method may be developed. Results obtained upon mixed fertilizers by the modified official method show an increase of potash recovered." The only recommendation made was that a further study be made of the volumetric and gravimetric cobalti-nitrite methods; and also of the modified official method by washing a weighed amount of the sample through filter paper, with hot water, to determine potash in the filtrate. These recommendations were adopted.

sisted in a further comparison of the J. L. Smith and the Modified Cobalti-Nitrite method as well as the making of acidity determination according to the Söchting and the Veitch methods. Three lots of acid soils from the Rhode Island and Ohio Stations were used for this purpose. The recommendation of the referee that the Modified Cobalti Nitrite method be made an optional official method for the determination of total potassium in soils was modified by the Committee on Recommendations to read that the method be further studied and was so adopted by the Association. The other recommendation of the

TABLE III.—INORGANIC PLANT CONSTITUENTS.

Separation of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>—Molybdate Method. Synthetic solution containing 2.00 per cent. Fe<sub>2</sub>O<sub>3</sub> and 3.98 per cent. Al<sub>2</sub>O<sub>3</sub>.

Analyst.	No. of determinations.	Per cent. Fe <sub>2</sub> O <sub>3</sub> .			Per cent. Al <sub>2</sub> O <sub>3</sub> .		
		Min.	Max.	Ave.	Min.	Max.	Ave.
W. H. Ross, Tucson, Ariz.....	3	1.98	1.98	1.98	4.44	4.48	4.46
H. B. Eggers, Newark, Del.....	4	1.94	1.96	1.96			
	3				4.42	4.90	4.61
R. O. Baird, Stillwater, Okla.....	3	2.16	2.16	2.16	3.46	3.50	3.48
O. M. Shedd, Lexington, Ky.....	5	1.99	2.02	2.01			
	4				4.04	4.06	4.05
W. H. McIntire, State College, Pa.....	1		2.14				
	2				3.92	4.86 <sup>2</sup>	4.39
J. S. Jones, Moscow, Idaho.....	3	2.28	2.28	2.28	4.16	4.28	4.21
F. W. Sherwood, W. Raleigh, N. C.....	3	2.06	2.10	2.08			
	2				4.08	4.22	4.15
O. B. Winter, E. Lansing, Mich.....	2	2.52 <sup>3</sup>	2.60 <sup>3</sup>	2.56			
	4				3.60	3.80	3.71
J. P. Aumer, Urbana, Ill.....	2	0.70 <sup>3</sup>	0.76 <sup>3</sup>	0.73	5.55 <sup>3</sup>	6.15 <sup>3</sup>	5.85
G. E. Boltz, Wooster, O.....	2	1.94	2.04	1.99			
	1				4.05		
R. M. Pinckney, Bozeman, Mont.....	3	1.78	1.92	1.83			
	7				4.57	5.53 <sup>3</sup>	5.19

Percentage Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> combined.

		Min.	Max.	Ave.
E. S. Erb, State College, Pa.....	2	11.06	11.20	11.13
A. T. Charron, Ottawa, Canada.....	3	6.04	6.28	6.16

Average of 27 determinations on above solution shows 2.04 per cent. Fe<sub>2</sub>O<sub>3</sub>.

Average of 26 determinations on above solution shows 4.12 per cent. Al<sub>2</sub>O<sub>3</sub>.

<sup>1</sup> THIS JOURNAL, 1, 409.

<sup>2</sup> Fe<sub>2</sub>O<sub>3</sub> present in the ignited precipitate.

<sup>3</sup> Omitted from the general average.

referee, that the study of the method for the quantitative estimation of the soil acidity be continued, was adopted.

A recommendation, introduced by Mr. Shedd, of Kentucky, that the referee on soils for 1911 be instructed to investigate a more accurate method for humus determination was adopted.

The closing report on the allied subjects of soils and fertilizer analysis was given by the referee on inorganic plant constituents, O. M. Shedd. The methods studied were the peroxid method for sulphur in plants (Table II) and the method for the separation of the ferric and aluminic oxides in an ash solution (Table III). The samples used were graham flour

the Association of Official Agricultural Chemists for several years, it was finally decided that the subject be brought to the attention of the International Congress of Applied Chemistry by the following resolution, adopted at the meeting of 1907:

"That the suggestion of the committee looking toward the ultimate adoption of the element system be approved, but that no state should discontinue the use of the terms now in use until such discontinuation is also approved by this Association, and that meanwhile the subject should be brought before the International Congress of Applied Chemistry in an effort to secure international agreement."

TABLE IV.—ANALYSES OF WATERS.

Expressed in Parts per Million.

Analyst.	SiO <sub>2</sub> .	SO <sub>4</sub> .	HCO <sub>3</sub> .	NO <sub>3</sub> .	Cl.	Fe.	Al.	Mn.	Ca.	Mg.	K.	Na.	Li.	NH <sub>4</sub> .	
No. 1.....	4.9	219.1	286.6	1.5	48.0	....	0.3	....	None	107.1	32.0	7.2	54.8	0.7	Traces
No. 2.....	2.82	223.75	309.57	44.16	1135.0	1.32	....	0.49	None	110.3	41.2	16.8	110.3	11.3	10.34
No. 3.....	4.45	219.85	281.5	2.52	49.75	....	0.33	....	Trace	108.25	31.05	6.55	55.9	0.67	0.088
No. 4 (a).....	5.0	216.33	271.45	42.24	49.70	2.19	....	0.65	None	108.65	30.98	6.71	54.75	0.83	0.119
No. 5 (b).....	6.3	211.9	....	1.99	52.0	....	1.19	....	0.94	116.51	39.59	6.88	56.46	1.07	0.069
No. 6 (c).....	6.03	237.6	274.5	1.10	53.1	3.94	....	None	None	104.1	22.34	4.72	35.66	0.65	0.128
No. 7.....	6.6	223.6	271.45	0.017	45.75	....	1.33	....	None	109.9	33.6	5.6	40.2	0.64	0.089
No. 8.....	3.1	220.1	302.0	1.00	57.1	9.8	....	....	....	119.0	41.2	4.6	42.5	....	1.1

Comments of Analysts.

(a) It seems to me that after silica has been determined by volatilization with sulphuric acid and hydrofluoric acid the residue of iron and aluminum should be dissolved in hydrochloric acid and the solution added to the filtrate from the digestion of the insoluble residue first obtained before that filtrate is made up to definite volume. Again, in the determination of K and Li a correction factor is used. It occurs to me that in the case of K particularly the correction factor should be somewhat dependent upon the particular aliquot portion used.

(b) In the evaporation of the original sample for silica determination a porcelain instead of a platinum dish was used.

(c) We evaporate the water in porcelain dishes instead of platinum. Iron is determined from an aliquot by the Zimmerman-Reinhardt method. The iron. We use these methods for iron and lime because we have found them more rapid and quite as accurate.

and linseed meal for the sulphur work and a synthetic hydrochloric acid solution for the separation of ferric and aluminic acid. The referee recommended that the peroxid method for sulphur in plants be made official, stating that the method had been before the Association since 1903, and had been found

The committee proposes to communicate with the secretary of the Eighth International Congress and request that the executive committee of that congress be asked to make provision for the full consideration of the matter.

Mr. J. K. Haywood presented a paper giving the results of cooperative work on mineral water analysis, which started a lively discussion. The methods used were those published in Bureau of Chemistry, *Bull.* 91 and *Circular* 52 and the results are shown in Table IV. The results are similar to those generally reported at the beginning of cooperative analytical work.

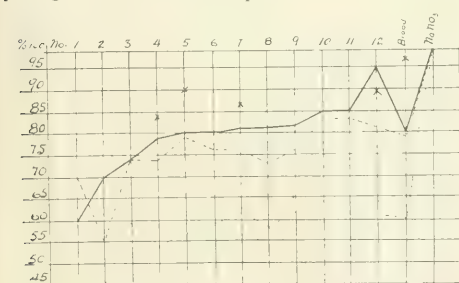
Thursday night the members and guests were entertained at a smoker given in their honor by the Washington Section of the American Chemical Society. The smoker was held at the Cosmos Club and was well attended and enjoyed.

On Friday the morning and afternoon sessions were devoted to food adulteration, and were mainly of a formal and routine character. At the beginning of the morning session Secretary Wilson, of the Department of Agriculture, delivered a short address on the work of the Association and the operation and enforcement of the Pure Food and Drugs Act.

After the afternoon session members and guests were invited to inspect the new laboratories of the Bureau of Chemistry, and considerable time was spent in examining the splendid equipment of the Bureau. The general arrangement of the floors and laboratories is shown by the following directory:

FIG. 1. NITROGEN AVAILABILITY.

Nitrogen from water-insoluble portion of commercial fertilizers. Results from pot experiments compared with figures by the modified alkaline permanganate method on similar samples.



— Average availability from three crops on bases of blood = 80%.  
Furnished by B. L. Hartwell and F. R. Pember.

- - - Modified alkaline permanganate method by C. H. Jones.

..... Original alkaline permanganate method by C. H. Jones.

× × Neutral permanganate method by J. P. Street.

satisfactory. The motion was carried. It was further ordered that the methods on the determination of ferric and aluminic acid be further studied before they were adopted.

The Committee on Unification of Terms for Reporting Analytical Results in Soils, Fertilizers and Ash reported through the chairman, Mr. R. J. Davidson, as follows:

The question of the unification of terms for reporting analytical results in soils, fertilizers and ash having been before

<sup>2</sup> A. O. A. C. Proceedings, 1908, p. 93 (*Bull.* 122, Bureau of Chemistry).

6TH FLOOR.			
Rooms 601-603	Bacteriological Laboratory	Dr. Stiles.	
607-608	Pharmacological Laboratory (Div. Drugs)	Dr. Salant.	
Room 610	Enzyme Investigation Laboratory	Dr. Hudson.	
Rooms 611-613	Animal Physiological Laboratory	Dr. Weber.	
Room 614	Nitrogen Section	Mr. Trescott.	
5TH FLOOR.			
Rooms 502-504	Microchemical Laboratory	Mr. Howard.	
	DIVISION OF DRUGS.		
Room 501	Essential Oils Laboratory	Mr. Nelson.	
Rooms 505-506	Drug Division Laboratory	Dr. Kebler.	
Rooms 507-508	Offices of Division	Dr. Kebler.	
Room 509	Drug Inspection Laboratory	Dr. Hoover.	
Rooms 511-512	Synthetic Laboratory	Dr. Emery.	
Rooms 513-514	Offices of the Chief Inspector	Mr. Campbell.	
4TH FLOOR.			
Rooms 413-414	General Offices of the Bureau.	Dr. Wiley.	
Room 407	Offices of the Chief Secretary of the Board	Dr. Dunlap.	

3RD FLOOR.		
Rooms 301-302	Sugar Laboratory (Constant Temperature Polaroscope Rooms are located on this floor ad- joining the Sugar Laboratory.)	Mr. Bryan.
Room 303	Dr. Wiley's Private Laboratory	Mr. Schreiber.
DIVISION OF FOODS.		
Rooms 304-308	Wash. Food Inspection Laboratory	Mr. Tolman.
Room 310	Offices of the Chief	Dr. Bigelow.
Rooms 311-312	In Charge of Chief of Division	Dr. Bigelow.
Room 313	Laboratory of Food Technology	Mr. Chace.
Room 314	Oil, Fat and Wax Laboratory	Mr. Bailey.
2ND FLOOR.		
" 201	Fermentation Laboratory (Div. Foods)	Dr. Lee.
MISCELLANEOUS DIVISION.		
Rooms 202-203	Cattle Food Lab. and General Extrac- tion Room	Mr. Bidwell.
Room 204	Insecticides Laboratory	Mr. McDonnell.
" 205	Trade Wastes Laboratory	Dr. Haywood.
" 206	Offices of Division	Dr. Haywood.
Rooms 207-209	Water Laboratory	Mr. Skinner.
211-214	Vegetable Physiological Laboratory	Dr. LeClere.
1ST FLOOR.		
" 101-106	Contracts Laboratory	Mr. Walker.
" 107-111	Leather and Paper Laboratory	Mr. Veitch.
" 112-114	Dairy Laboratory	Prof. Patrick.
BASEMENT.		
" 10 & 11	Fruit Investigation Lab. (Div. Foods)	Mr. Gore.

Cold Storage Plant of the Bureau is located in the northeast corner. Machine Shop, Sample Room, Glassblower's Room and Milling Room will also be found on this floor.

Friday night the members were the guests of The City of Washington Branch of the American Pharmaceutical Association at a meeting to discuss "The Pharmacopoeia of the United States." Dr. H. W. Wiley presented a communication on "The United States Pharmacopoeial Convention and the Future of the [Pharmacopoeia]," which was discussed by prominent members of the American Pharmaceutical Association.

The meeting closed on Saturday, November 12th.

#### EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, 1912.

Satisfactory progress is being made by the officers and committees of the Eighth International Congress. The presidents and vice-presidents of the Sections and Sub-sections have been appointed, and a list of them is given below. Their first meeting was held November 21st, at the Waldorf-Astoria, in New York City, under the presidency of Dr. Wm. H. Nichols, President of the Congress, and the Honorary President, Professor E. W. Morley. The list follows:

SECTIONS AND SUB-SECTIONS AND THEIR PRESIDENTS AND VICE-PRESIDENTS. NAMES OF PRESIDENTS ARE GIVEN FIRST, THE NAMES OF THE VICE-PRESIDENTS FOLLOWING.

1. Analytical Chemistry—Dr. W. F. Hillebrand, Washington, D. C.; Prof. H. P. Talbot, Boston, Mass.
2. Inorganic Chemistry—Prof. C. L. Parsons, Durham, N. H.; Prof. Charles Baskerville, N. Y. City.
- 3a. Metallurgy and Mining—Prof. J. W. Richards, So. Bethlehem, Pa.; Dr. J. B. F. Herreshoff, N. Y. City.
- 3b. Explosives—Prof. C. E. Munroe, Washington, D. C.
- 3c. Silicate Industries—Dr. A. S. Cushman, Washington, D. C.; Dr. Karl Langenbeck, Boston, Mass.
4. Organic Chemistry—Prof. M. T. Bogert, N. Y. City; Prof. W. A. Noyes, Urbana, Ill.
- 4a. Colors—Hon. H. A. Metz, N. Y. City; Eugene Merz, Esq., N. Y. City.
- 5a. Industry and Chemistry of Sugar—Dr. W. D. Horne, Yonkers, N. Y.; Dr. F. C. Wiechmann, N. Y. City.
- 5b. Industry and Chemistry of India Rubber and Other Plastics—Dr. L. H. Bickeland, Yonkers, N. Y.; C. C. Goodrich, Esq., N. Y. City.

- 5c. Fuels and Asphalt—Dr. David T. Day, Washington, D. C.; Dr. F. Schniewind, N. Y. City.
- 5d. Fats, Fatty Oils and Soaps—David Wesson, Esq., N. Y. City; Dr. Martin H. Ittner, Jersey City, N. J.
- 6a. Starch, Cellulose and Paper—A. D. Little, Esq., Boston, Mass.; Dr. T. B. Wagner, Chicago, Ill.
- 6b. Fermentation—Dr. Francis Wyatt, N. Y. City; Dr. Robert Wahl.
7. Agricultural Chemistry—Dr. F. K. Cameron, Washington, D. C.; Prof. H. J. Wheeler, Kingston, R. I.
- 8a. Hygiene—Prof. W. T. Sedgwick, Boston, Mass.; Dr. L. P. Kinnicutt, Worcester, Mass.
- 8b. Pharmaceutical Chemistry—Prof. J. P. Remington, Philadelphia, Pa.; Prof. V. Coblentz, N. Y. City.
- 8c. Bromatology—Dr. W. D. Bigelow, Washington, D. C.; Dr. A. L. Winton, Chicago, Ill.
- 8d. Physiological Chemistry and Pharmacology—Prof. J. J. Abel, Baltimore, Md.; Prof. W. J. Gies, N. Y. City.
9. Photochemistry—Prof. W. D. Bancroft, Ithaca, N. Y.; R. J. Wallace, Esq., St. Louis, Mo.
- 10a. Electrochemistry—Prof. W. H. Walker, Boston, Mass.; Prof. C. F. Burgess, Madison, Wis.
- 10b. Physical Chemistry—Dr. W. R. Whitney, Schenectady, N. Y.; Prof. Alexander Smith, Chicago, Ill.
- 11a. Law and Legislation Affecting Chem. Industry—(No officers elected as yet).
- 11b. Political Economy and Conservation of Natural Resources—Prof. J. A. Holmes, Washington, D. C.; Prof. C. R. Van Hise, Madison, Wis.

#### WOOD TURPENTINE ASSOCIATION.

A meeting of the Wood Turpentine Association was held at Jacksonville, Florida, on September 24th, and was attended by representatives of a large number of plants engaged in the manufacture of high-grade wood spirits of turpentine and pine oil.

The main object of the association at the present time is to improve the quality of their products and to establish uniform standards to which all the members of the association will bring their products before placing them on the market. The officers of the association are: Dr. J. E. Teeple, of New York, President; Mr. A. J. Grant, of Orlando, Florida, Secretary.

#### PERSONAL NOTES.

William Henry Brewer, professor emeritus in the Sheffield Scientific School of Yale University, died at New Haven, Nov. 2d. He was one of the most distinguished members of Yale's scientific faculty. He was 91 years old. He was graduated from Yale fifty-eight years ago, continuing his studies with prolonged residence at Heidelberg, Munich and Paris. During the Civil War period he was professor of chemistry in the College of California, which he left about 1865 to take the chair of agriculture at Yale. Professor Brewer had served on more than forty government and state commissions. He was chairman of the commission organized at the request of President Roosevelt to draw up a plan for a scientific survey of the Philippine Islands. During his term in office at Yale he declined the presidency of some thirty agricultural colleges in various parts of the country. His relaxation was exploration and mountain-climbing.

Dr. Henry Wurtz, chemist and scientist, died November 11th at his home, in Brooklyn, in his 83d year. He was born at Easton, Pa., and was a graduate of Princeton University and of the Massachusetts Institute of Technology. He was the author of many scientific treatises and was the first investigator to



prove the existence of gold in sea water. He held many Government positions.

**Warning.**—A person calling himself "John Pearson" has been going about among members of the *Chemical Society* and the *Society of Chemical Industry*, representing that he is a relative of the undersigned, in needy circumstances, and attempting to negotiate loans, etc., etc., on that basis. The relationship story is utterly false. (Signed) WATSON SMITH,

Editor of the "*Journal of the Society of Chemical Ind.*"

A man giving his name as John Pearson and talking and acting like an Englishman was in Columbus, O., recently, asking assistance from chemists, and stating that he was injured in a fire in Toledo, O., about six weeks ago. He stated that he was a relative of Mr. Schweitzer, of the Society of Chemical Industry, and also claimed acquaintance with Dr. Arthur Noyes, Dr. Wm. A. Noyes, and other prominent chemists. Dr. Schweitzer has disavowed any knowledge of this man.

## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**973,776. Process of Extracting Metals from Their Ores.** WILLIAM E. GREENWALT. Patented Oct. 25, 1910.

This invention relates generally to process of extracting metals from their ores but it will be described more particularly in its application to copper ores, and to ores containing copper with variable quantities of gold, silver, lead, nickel, cobalt, zinc, and other metals.

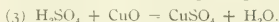
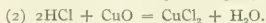
Copper ores usually contain variable quantities of other metals, and these metals cannot be recovered by any one of the wet methods now in use. One and sometimes two additional treatments are necessary to extract the gold and silver occurring with the copper, and the lead is invariably lost. One of the essential difficulties with acid process has been that the acid is usually too expensive to admit of extended use in mining

The amount of acid which is necessary to provide, in any acid process, is considerably more than that combining with the copper, and all the acid is irrecoverably lost when iron is used as the precipitant. Theoretically, 88.8 pounds of iron are required to precipitate 100 pounds of copper from sulfate solutions. In practice, it takes from 200–300 pounds of scrap iron. Here, again, a large expense is incurred in providing iron with which to precipitate the copper. The fundamental difficulty, therefore, in treating copper ores in the past by these methods has been the excessive cost of the materials.

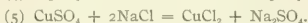
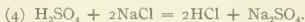
In this electrolytic process, the copper is dissolved by dilute acid chlorid solutions, and then precipitated by electrolysis, while at the same time the acid, which was combined with the copper, is multiplied and again regenerated as free acid, at the expense of sulfur dioxide and water. Salt is the only chemical to provide, which is not usually contained in the ore. Sulfur dioxide, derived from roasting sulfid ore, is the active chemical consumed. Theoretically, the chlorine in the salt is not consumed; nevertheless, in practice, about one-eighth pound of salt should be provided for every pound of copper produced.

The oxid, carbonate, and silicate ores of copper may be treated without roasting. The sulfids are roasted. If the ore is roasted, salt may be added during the roasting.

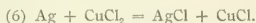
In working the process, the ore, after being suitably crushed, is placed in large leaching vats for chemical treatment. The first step in the chemical process consists in combining chlorine, generated from metal chlorids by electrolysis, with sulfur dioxide produced by roasting concentrates or sulfid ore, in the presence of water, to form acid. This may be shown by the following reactions:



Both sulfuric acid and copper sulfate react with common salt to form hydrochloric acid or cupric chlorid, so that neither the sulfuric acid nor the copper sulfate could exist in the solution. These well-known reactions are:



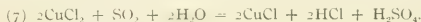
Cupric chlorid, when warm and in the presence of other metal chlorids, acts readily on silver and its compounds in the ore to form silver chlorid, thus:



From 80–90 per cent. of the silver may, in this way, be extracted with the copper, especially if the ore is given a chloridizing roast. Lead is similarly extracted. If the ore contains considerable silver it is desirable to leach with a fairly concentrated solution of base metal chlorids.

The solubility of chlorid in water is limited. By the indirect method of combining the chlorine with sulfur dioxide and water to form acid, any desired strength of acid solution may be obtained from the copper, and a chlorine solution of sufficient strength for the gold.

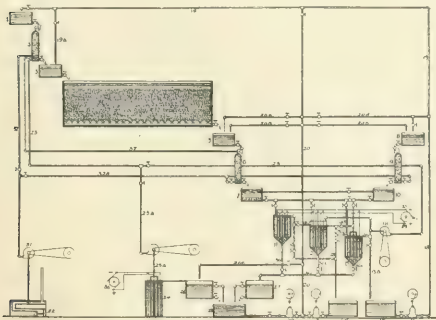
The cupric chlorid solution issuing from the leaching vat is saturated with sulfur dioxide obtained from roasting sulfid ore. This converts the cupric chlorid into the cuprous chlorid, thus:



The object of this is:

First, the electric current deposits twice as much copper, theoretically, per ampere, from a cuprous as from a cupric solution, and with an expenditure of only 65 per cent. of the energy per unit of copper.

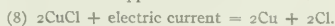
Second, the sulfur dioxide, reacting with cupric chlorid and water, produces large quantities of acid. A molecule of acid is in this way regenerated for every molecule of cupric chlorid reduced to cuprous chlorid. For every pound of copper reduced



districts, which are ordinarily far from the source of acid supply. It takes approximately 1.5 pounds of sulfuric acid to dissolve one pound of copper as sulfate. If hydrochloric acid is used, it takes approximately 0.6 pound of acid to extract one pound of copper as cuprous chlorid, and 1.1 pound as cupric chlorid. Much of the acid, whether sulfuric or hydrochloric, combines with the base elements of the ore and serves no useful purpose.

from the cupric to the cuprous condition, 1.4 pounds of acid regenerated.

Third, the excess of sulfur dioxide combines with the chlorine liberated during electrolysis of the cuprous chloride to precipitate the copper, thereby again regenerating 1.4 pounds of acid for every pound of copper reduced from the cuprous condition to metallic copper. The reactions are:



These reactions may take place in the electrolyzer. Usually the excess of chlorine will be conducted to a separate chamber where it may combine with the sulfur dioxide in the solution.

Fourth, the above reactions rise to an electromotive force working with the current, thereby reducing the necessary voltage in the deposition of the copper.

Fifth, it dispenses with the necessity of diaphragms in the electrolyzers, although at times diaphragms may be desirable.

Sixth, it is possible, by this method, to extract the other valuable metals from the ore, with the copper and with the same solution. This is not possible when working on a sulfate basis.

Seventh, insoluble anodes, decomposing chloride solutions, are vastly more durable than when decomposing sulfates. Graphitized carbon electrodes have proved effective for the decomposition of chlorides, while the production of a suitable insoluble anode for the decomposition of sulfate may still be regarded as one of the unsolved problems of electrometallurgy.

972,947. Electrolytic Decomposition of Solutions. CLINTON P. TOWNSEND, of Washington, D. C. Patented Oct. 18, 1910.

This invention relates to the electrolytic decomposition of solutions, and particularly to a process of collecting the products of such decomposition.

According to the invention, one of the products of the electrolysis, or a secondary product resulting from the action of the primary product upon the electrolyte, or upon the immiscible liquid, hereafter mentioned, is collected in, under and above an immiscible liquid, which serves several important functions.

The cell comprises a central compartment, *B*, containing an anode, *D*, and one or more lateral or cathode compartments, *C*, shown as two in number, the lateral compartments being separated from the central compartment by the cathodes and diaphragms.

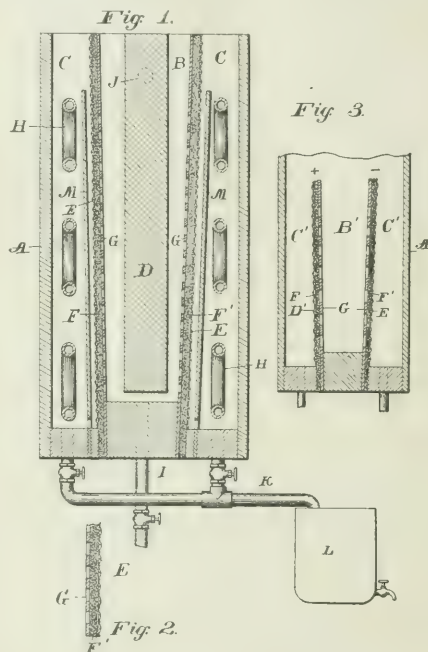
*F F'* are diaphragms of asbestos or other suitable pervious material supported between the perforated sheet or wire gauze *E*, and the perforate or pervious plate *G*. As shown, *E E* are of metal and constitute the cathodes of the cell. The plates *G*, which may be of hard rubber or earthenware, hardened asbestos or any suitable material, are preferably non-conducting and serve to support the diaphragm proper; they may, of course, be dispensed with, if the diaphragm be so treated as to be capable of supporting itself. They are shown as imperforate in their upper portions. It will be noted that the cathodes are shown as inclined slightly from the vertical, but such inclination is not essential.

*M* represents a sheet of metal, as iron, adjacent and approximately parallel to the cathode. This plate terminates a slight distance above the bottom of the cathode compartment and below its top, for a purpose hereinafter described.

*H* is a coil suitably connected and employed for heating or cooling the liquid in the cell to maintain its temperature at any desired point.

As illustrated, the cathode compartments *C* are somewhat deeper than the central or anode compartment, and are provided with valve-regulated drain pipes communicating with a main conduit, *K*, leading to the tank *L*, from which the solution may be withdrawn as desired.

In operation, the central compartment is filled with sodium chloride solution, and a continuous flow is preferably maintained through this compartment from below upward, the inlet *I* and the outlet *J* being provided to this end. The lateral compartments are filled to a higher or lower level with a liquid which is substantially immiscible with water or aqueous solutions and inert toward the products of electrolysis liberated



in contact therewith, or the secondary products resulting from the oxidation or other chemical modification of said products. Of such liquids, the non-saponifying oils may be taken as an example. Upon the passage of the current chlorine is liberated at the anode and sodium at the cathode. The chloride escapes from the cell and may be collected and used as desired. The sodium is set free at the cathode and is in part or entirely oxidized by the solution in the diaphragm or percolating through the diaphragm. The caustic solution so formed under the oil detaches itself freely from the cathode and is withdrawn from the cell through the pipe *K*. The hydrogen which results from the reaction escapes upward through the narrow space between the cathode and the plates *M*, thereby inducing a strong circulation of the oil, which further aids in detaching the globules of caustic solution, thereby removing them quickly from the field of the electrolytic action.

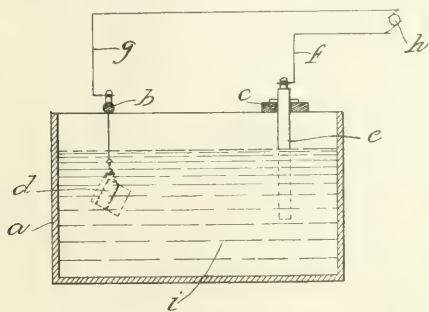
971,641. Art of Enameling Metals. GEO. L. RICE AND BENJ. W. GILCHRIST, of Woodhaven, N. Y. Patented Oct. 4, 1910.

This invention relates to the art of enameling metal and particularly to the art of enameling household utensils and other articles of manufacture or merchandise composed of iron or steel.

In the accompanying illustration is shown at *a* an ordinary electrolytic cell provided with the usual cathode and anode supports *b* and *c*, and from the cathode support *b* is suspended a utensil, *d*, which constitutes the article to be enameled, and

from the anode support *c* is suspended the usual anode 3, and connected with the parts *b* and *c* or through said parts with the parts *d* and *e* are the usual circuit wires *f* and *g* which connect with a generator, *h*, or other source of electricity.

The cell  $a$  contains an electrolyte,  $i$ , of which sulfur and a salt of metal or metals form a part, and the operation of this apparatus will be the same as that of all similar apparatus of this class. In this operation there is a film or covering of material deposited on the utensil  $d$ , and this film or covering contains



sulfur which may be present either in the free or combined state.

The invention is particularly designed for use in enameling various utensils or articles composed of iron or steel, and in practice we prefer that the electrolyte in the cell *a* shall contain salts of magnetic metals and sulfur.

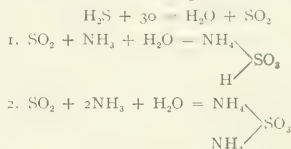
In the enameling of articles composed of iron or steel, as this process has heretofore been produced, it has been found difficult to unite the enamel with the body of the utensil or article in such manner as to produce a perfect union, and the enamel easily shells off or breaks off, but with the process the sulfur in the magnetic covering or coating which is first placed on the utensil or article to be enameled enables the enamel to adhere to the body of the utensil or article and to practically form an integral part thereof, or in other words the union between the iron or steel body, the magnetic film or coating and the enamel is such that these parts cannot be separated, and while the enamel may be broken by violent or rough usage it will not separate from the metallic body.

973,164. Process of Obtaining Ammonium Salts from Gas.  
KARL BURKHEISER, of Aix-la-Chapelle, Germany. Patented  
Oct. 18, 1910.

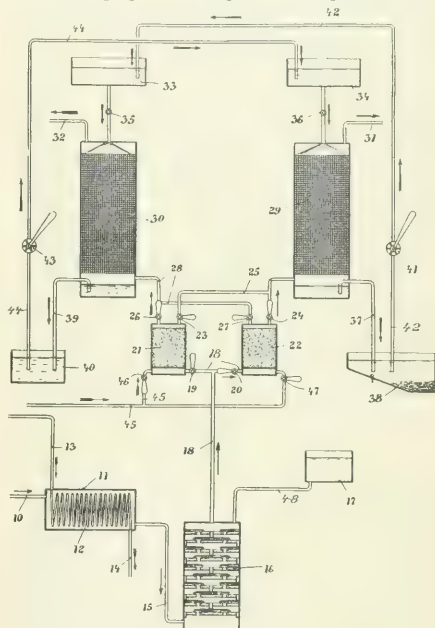
This invention relates to a process of obtaining ammonium salts from gases, such as illuminating gas or coke-oven gas, in a simple and economical manner. For this purpose the sulfur and ammonia in the gas are caused to so interact to directly produce ammonium sulfite or ammonium sulfate.

In carrying out the process, the gas passes over a substance which is capable of giving off oxygen, such as roasted bog iron ore, said substance being heated to a temperature at which condensation of the water contained in the gas is prevented, said temperature being under normal conditions 60-70°C. The oxidizing substance is either continuously regenerated by adding air or pure oxygen to the gas passing thereover, or it is intermittently regenerated by passing alternately gas and air currents over said substance. If the oxidizing substance is continuously regenerated and heated to the temperature of oxidizing sulfurfretted hydrogen, the latter is decomposed into sulfurous acid and water, while at higher temperatures and with a sufficient supply of oxygen, sulfuric anhydride is formed. If, however, the oxidizing substance is intermittently regenerated, there occurs first an oxidation to sulfur compounds which are subsequently higher oxidized when oxygen is passed over said

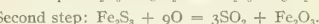
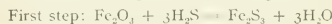
compounds. The sulfur dioxide or sulfur trioxide reacts on the ammonia contained in the gas with which it will form acid or neutral sulfite or sulfate of ammonia. The reactions taking place with a continuous regeneration of the oxidizing substance yield, in the first case, an acid sale, while in the second case, a neutral salt is obtained, owing to the combination of twice the quantity of ammonia with the same quantity of sulfurous acid, the reactions being as follows:



For illustrating the reactions that take place when intermittently regenerating, it may be assumed that oxid of iron be used as oxidizing agent. During the first step the sulfuretted



hydrogen combines therewith, while during the second step the oxidizing substance is regenerated and the sulfur oxygen compound is formed according to the following formulae:



Owing to the contact between the sulfur oxygen compounds thus formed and the ammonia, the above-described reactions will either yield an acid or a neutral salt according to the quantity of ammonia present.

The accompanying drawing illustrates a diagrammatic elevation of a plant for carrying out the process.

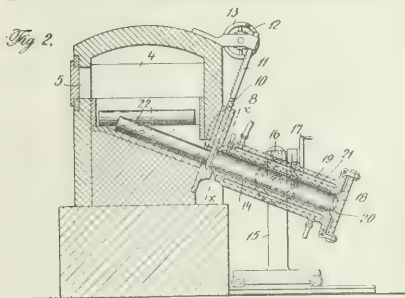
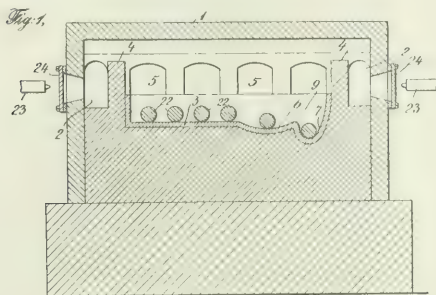
972,561. Method of and Apparatus for Producing Coated Metal Objects. JOHN F. MONNOT, of New York, N. Y. Patented October 11, 1910.

This invention relates to methods of, and apparatus for, producing coated metal objects, particularly compound ingots



comprising unlike metals weld-united, and consists in means whereby a billet or object to be coated may be heated to a high temperature while immersed in a bath of flux or like fused protective material, and may be transferred to a mold while still submerged in such protective material, and then may have a layer of molten metal cast about it and united to it as the metal so cast solidifies.

The invention consists in the process comprising the heating of an object to be coated, under protection of an enveloping



bath of fused protective material, transferring the object while still so enveloped to a suitable mold, and casting a body of molten metal or other suitable material into said mold and against the surface of the heated object and causing the metal so cast to solidify against such object, the metal so cast being cast through a deep body of the molten protective material within the mold and displacing such material, the latter therefore serving as a wiping material for the molten metal, whereby the molten metal as cast is purified and freed from entrained and occluded gases, oxid impurities, etc.

## INDUSTRIAL AND TRADE NOTES.

### A BRITISH RADIUM DISCOVERY.

[From Consul Frederick I. Bright, Huddersfield, England.]

It is reported that a new process of extracting radium from pitchblende produced at Cornish mines has been adopted, by means of which more radium can be extracted in two months than in one year by the present methods employed on the continent of Europe. The following statement is from a Yorkshire paper:

Sir William Ramsay received a party of gentlemen at the radium works, established in Limehouse by a subsidiary company of the St. Ives Consolidated Mines (Limited), and an-

nounced to them that for the first time radium had been produced in Great Britain from British ore. Up to now 550 milligrams of pure radium have been produced, and the process adopted by Sir William Ramsay and his chief assistant, Mr. Norman Whitehouse, is so rapid that radium which is extracted in two months at Limehouse could only be extracted in a year by the latest method in use on the Continent.

Those who visited the works were shown 2,600 milligrams of 10 per cent. radium, the present market price of which is about 1/20 per milligram. It is stored in a specially constructed safe lined with lead and asbestos, and remarkable precautions are taken to insure its safety.

In an interview, Sir William Ramsay said that there was every likelihood of the rate of production he had spoken of continuing. But there was a great demand for it from hospitals and doctors. Its curative qualities were being gradually discovered, and there would be no difficulty in disposing of all they produced.

### POWDERED SUGAR CANE.

[Extract from a British Guiana paper, forwarded by Consul Arthur J. Clare, Georgetown.]

A patent has been applied for in one of the neighboring colonies in relation to "improvements for treating sugar cane." The invention involves the separation of the canes into their two principal structural parts, pith and woody fiber, by mechanically reducing the canes to fine shreds and then completing the separation by a screening or sifting operation and separately collecting the two parts, all this with the retention of the natural juices. The stalks are passed end-wise through rotary cutters by which they are shredded into a mass in which the pith exists in sawdust-like, particles and the fiber in fine filamentary shreds. The sugar cane, thus reduced to dust and shreds, is intended for export in this condition, the idea underlying the enterprise being to escape the duty chargeable on sugar on admission to the United States.

### BRIQUETTING OF IRON ORES.

[From Consul F. I. Bright, Huddersfield, England.]

At a recent meeting of the British Iron and Steel Institute the following rules were recommended for the successful briquetting of iron ores:

- (1) The iron ore briquettes must have a certain resistance against mechanical influences. They must resist a pressure of not less than 2,000 pounds per square inch, and when dropped from a height of 10 feet on a cast-iron plate they must not fall into dust, although they may break into pieces.
- (2) They must resist heat. Heated to 900° C., they may commence to sinter, but they must not disintegrate into small fragments.
- (3) They should be capable of being placed in water for a certain time without softening.
- (4) They must resist the influence of steam at 150° C., without crumbling.
- (5) They must possess a certain amount of porosity in order to allow the carbon monoxide in the blast furnace to penetrate the interior of the briquette, and to exercise its beneficial reducing influence.
- (6) The binding material, if any is used, should not contain noxious substances (sulphur, arsenic) to such an extent as to be injurious to the quality of the pig iron produced.
- (7) The cost of producing briquettes should not exceed the difference in the prices between lump ore and fine ore.

### POTASH SALTS IN GALICIA.

[From Consul-General Charles Denby, Vienna.]

The operations of the syndicate formed for exploiting the

potash salt deposits at Kalusz, in the Austrian Province of Galicia, continue to attract wide attention.

Up to the present the mining operations are developed only within an area of 1,148 by 1,800 feet, wherein four shafts have been sunk of less than 920 feet in depth. The quantity of potash (kainit, sylvin, and sylvinite) produced is regarded as a guaranty of future success. According to expert estimate, a supply of 33,000,000 pounds per annum may be obtained from existing shafts for eighteen years, but it is believed that greater depth of borings will show much greater productiveness. This hypothesis is based on the geological resemblance of the Kalusz field to the fields at Stassfurt, Germany, where kainit, sylvin, sylvinite, and karnallit have been found only in shafts over 980 feet deep, the various shafts in Germany in nearly every case running from that to a depth of 2,438 feet.

It is the purpose of the Austrian syndicate not only to dig deeper, but to open additional shafts and to introduce better mining methods.

Up to the present time the Kalusz field has produced kainit and sylvinite chiefly, the kainit containing uniformly 12 per cent. to 15 per cent. of potash. During the years 1904 to 1908 the quantity of kainit sent from Kalusz to market amounted to 122,260,000 pounds; for the last of those years the amount was 24,840,000 pounds, valued at \$35,000. The reports for 1909 are not available.

Austria is annually importing an increasing quantity of chloride of potassium from Germany, *viz.*, 8,800,000 pounds in 1902 and 154,000,000 pounds in 1909. It is the plan of the Austrian syndicate not only to supply the Austrian demand, but to compete with Germany in foreign fields, and it is believed that, by cutting the present German monopoly prices, the demand can be largely increased.

Owing to the feature of the law of Austria which forbids the manufacture of mineral salts by private parties, the Kalusz field is to be worked under the form of a lease, the syndicate delivering the salt to the Government at a fixed price. The Government will erect and operate a factory at Kalsuz for its preparation for market. There are many features of the proposed joint working of the Government and the syndicate which are still to be determined, *viz.*, contract price for delivery of salt by the syndicate, terms of lease of additional territory, terms for syndicate participation in manufacture, etc. The syndicate, however, is a powerful one; financially it is equal to a great undertaking, and it has the support of a person of high rank in its dealings with the Government.

Offers from foreign countries to furnish capital and participate in the syndicate's operations have been received and rejected. It is the firm intention of the interested parties to maintain the enterprise as a purely Austrian undertaking. Herein lies the greatest advantage to the American purchasers, namely, a large supply from works independent of the German monopoly, at competitive prices.

#### SMELTING BY ELECTRICITY.

[From Consul P. Emerson Taylor, Stavanger, Norway.]

The Electro-Metallurgical Commission has completed its work and filed its report. In speaking of the work of the commission Professor Farups, of the University of Christiania, one of the members, says:

It is quite possible for us, in electric smelting of iron ore, to compete with smelting ovens of the old type in other countries. The iron ore is no more expensive here than in other places, and Norway is richer in electric energy, and electric power here is much cheaper than in other countries. Besides, we have very good export seaports, with our waterfalls and electric power close to the sea. Should the electric smelting of iron and steel, in spite of all this, become more expensive than smelting by the old methods, it will still be able to compete with the old method

of smelting because of the much finer quality of the product. In Sweden, where the new electric smelting ovens have been installed, the results show that the new method is a success and in an advanced stage of progress, and Norway will, with her electric power and transportation facilities, have many advantages over Sweden.

#### PETROLEUM OIL GUSHER.

The Palmer Oil Co. brought in another gusher Nov. 1st. Its well No. 3 was finished a week ago and put on the pump. From the first it is reported to have yielded over 200 barrels per day, while the veins in the oil sands were being opened up. Finally it came in as a gusher, flowing over 700 barrels with tremendous gas pressure. President Frank L. Brown, in a telegram, says: "It gives every indication of opening up into a bigger production than either well No. 1 or No. 2. Well No. 1 flowed constantly for almost two years at over 1,500 barrels a day. Last July well No. 2 came in, producing 300 barrels a day while it was being cleaned out, and then started to flow at the rate of 8,000 barrels a day—producing in August over 230,000 barrels. In September this well was shut off until the big storage tanks can be completed, but will be turned on again in a few weeks. With its three completed wells all gushers, the Palmer company can produce over 10,000 barrels a day.

"Because of its heavy production of oil the Palmer Company has joined with the Palmer Junior Oil Co. in building its own pipe lines to tidewater at Avalon, Cal., where it will have its own dock facilities and reservoirs capable of storing 1,500,000 barrels of oil. The pipe line will be completed by Jan. 1st, when these two companies will begin delivering their oil through their own pipe line, by their own tank steamers to San Francisco and other markets."

The American Viscose Company is building a new artificial silk factory at Chester, Pennsylvania. This Company is practically owned by Samuel Courtauld & Company, Ltd., London, England. It is capitalized at \$250,000 and is a Pennsylvania corporation. The Treasurer of the Company is William M. Kitzmiller, 144 East Washington Lane, Philadelphia, Penna.

#### PURCHASE OF IRON MINES.

All the Corrigan-McKinney mines on the Gogebic range were inspected recently by officials of the U. S. Steel Corporation, which is in negotiations for the purchase of all the mining and furnace interests of this company.

On this range its holdings consist of the Colby, Winona and Iron-ton, the three mines producing this year over 500,000 tons, though now closed down until the first of the month. The company also has large holding on the Menominee and Mesabur ranges, being the largest ore producers in the Lake Superior district outside the trust.

The deal, if consummated, will involve over \$20,000,000 in mine value, aside from any furnace interests at Cleveland and elsewhere.

#### MONAZITE AND ZIRCON PRODUCTION.

[From advance chapter of Mineral Resources of United States, by the Geological Survey.]

There is a constant demand for minerals carrying thorium for the manufacturer of incandescent gas mantles. A large number of such minerals are known to the mineralogist, though only one, monazite, has been found in quantities large enough to supply the commercial demand. Two other minerals that carry a large percentage of thorium—thorianite and thorite—have been obtained in small quantities from Ceylon.

Monazite is a phosphate of cerium, lanthanum, praseodymium, and neodymium containing a variable percentage

of silica and thorium. Its content of thorium ranges from less than 1 per cent. to more than 20 per cent. The quantity in monazite used for commercial purposes ranges from 3 to 9 per cent. In color monazite ranges from grayish to yellow, reddish, brownish, or greenish. Its luster is resinous and is especially brilliant on cleavage faces. It is opaque to translucent or subtransparent. Its specific gravity ranges from 4.9 to 5.3 and is generally over 5, so that it is readily concentrated by ordinary methods of washing. It is brittle, having a hardness of 5 to 5.5. Monazite generally occurs in small crystals with brilliant faces in the original rock matrix. When set free from the rocks and deposited in gravel beds by streams these crystals are rounded by attrition.

The world's sources of supply of monazite for many years have been Brazil and the United States. The Brazilian output (\$225,000 worth shipped from Bahia in 1908) is shipped to Germany, Austria, and England for manufacture into thorium salts. The greater part of the monazite produced in the United States is used in this country, though small quantities are exported annually. For a number of years past the supply has come from North Carolina and South Carolina, but it is probable that Idaho will add materially to the production hereafter. Deposits of monazite exist in other Western States and in Georgia and Virginia.

Practically all the monazite of commerce is derived from placer or gravel deposits. Unsuccessful attempts have been made to extract it from its original rock matrix on a commercial scale in North Carolina. Monazite placer deposits are worked like gold placer deposits, by sluicing and hydraulic mining, and the crude sand obtained is further cleaned on concentrating tables or by electro-magnetic machinery. In the United States the final cleaning of monazite before shipment is accomplished by three different types of electro-magnetic cleaning machines. These are especially adopted forms (1) of the Wetherill, in use by the German American Monazite Company, (2) a machine devised by the Carolinas Monazite Company, and (3) a new type made and patented for the Centerville (Idaho) Mining and Milling Company. These machines can be adjusted to clean the sand to 95 per cent. monazite, though the shipping grade is not generally so carefully cleaned.

The statistics of the production of monazite in the United States have been collected cooperatively by the Bureau of the Census and the United States Geological Survey. The production of crude monazite sand amounted to 1,976,320 pounds, averaging about 25 per cent. monazite. The crude concentrates yielded 541,931 pounds of refined sand, whose value before cleaning was \$65,032 or 12 cents per pound. Of this, 391,068 pounds, valued at \$46,928, came from North Carolina, and 150,863 pounds, valued at \$18,104, from South Carolina. The value of 12 cents per pound placed on the monazite is the rate paid the miners per pound of refined sand obtained by electro-magnetically cleaning their crude concentrates. It does not represent the value of the refined material, but of the quantity of crude concentrates necessary to yield 1 pound of refined monazite. The cost of cleaning is not included. The average price of crude monazite concentrates was  $3\frac{1}{2}$  cents per pound.

The following table gives the United States production and value of monazite from 1893 to 1909, inclusive; of monazite and zircon in 1903; of monazite, zircon, gadolinite, and columbite in 1904; of monazite, zircon, and columbite in 1905; of monazite and zircon in 1906 and 1907; and of monazite in 1908 and 1909.

The production of monazite in the United States in 1909 was, as usual, confined to North Carolina and South Carolina. Some mining and cleaning of monazite was done at Centerville, Idaho, but none of the sand was placed on the market. The company operating in this region is holding its output with the expectation that monazite will have an increased value through the

discovery of some use for its other constituents than thorium. An extensive series of tests are being made with this in view.

Year.	Quantity.	Value.
1893.....	130,000	\$7,600
1894.....	546,855	36,193
1895.....	1,573,000	137,150
1896.....	30,000	1,500
1897.....	41,000	1,980
1898.....	250,776	13,542
1899.....	350,000	20,000
1900.....	908,000	48,805
1901.....	748,736	59,262
1902.....	802,000	64,160
1903.....	865,000 <sup>a</sup>	65,200
1904.....	745,999 <sup>b</sup>	85,038
1905.....	1,352,418 <sup>c</sup>	163,908
1906.....	847,275 <sup>d</sup>	152,560
1907.....	548,152 <sup>e</sup>	65,800
1908.....	422,646	50,718
1909.....	541,931	65,032

<sup>a</sup> Including 3,000 pounds of zircon, valued at \$570.

<sup>b</sup> Including the small production of zircon, gadolinite, and columbite.

<sup>c</sup> Including a small quantity of zircon and columbite.

<sup>d</sup> Including 1,100 pounds of zircon, valued at \$248.

<sup>e</sup> Including 204 pounds of zircon, valued at \$46.

The production of refined monazite in the United States in 1909 was greater by 119,285 pounds in quantity and \$14,314 in value than in 1908. This increase was due to larger outputs in both North Carolina and South Carolina. The production was less by 6,017 in quantity and \$722 in value than in 1907 and was considerably smaller than in 1906.

According to the Bureau of Statistics of the Department of Commerce and Labor, there were 69,988 pounds of monazite and thorite, valued at \$8,324, and 17,549 pounds of thorium oxide and other salts, not nitrate, valued at \$19,596, imported into the United States during 1909. The imports of thorium nitrate were large, and are given, along with those of the preceding six years, in the following table:

Year.	Quantity.	Value.
1903.....	64,520	\$232,155
1904.....	58,655	249,904
1905.....	52,378	269,504
1906.....	40,090	139,929
1907.....	51,441	152,666
1908.....	65,289	173,239
1909.....	127,833	236,057

The imports of thorium nitrate for 1909 were but little less than twice as great as the imports for any one of the six preceding years. The price per pound in foreign markets as deduced from the table was only \$1.85, as against \$2.65 in 1908 and \$2.97 in 1907. If the imports of oxide of thorium and other thorium salts, not nitrate, are added to that of the nitrate, it will be seen that the quantity of manufactured thorium salts imported in 1909 was considerably over twice as great as in any previous year. According to the London Times, the price of thorium nitrate was dropped from \$2.81 per pound to \$2.37 and then to \$1.72 by the Austrian Welsbach Company. This was done in retaliation for the breaking of a certain unwritten agreement between the Welsbach Company and the German Thorium Convention. It is said with the method of extraction used by the thorium convention thorium nitrate costs about \$1.94 per pound, while the Austrian method is less expensive. With a 3 per cent. discount on the \$1.72 rate, making \$1.67 per pound, the Welsbach Company disposed of some 145,464 pounds of thorium nitrate in a few days. The thorium convention was greatly embarrassed, since the contracts with its customers called for the advantage of low market rates. The convention placed its price at \$2.05 per pound. It is not known whether a new understanding will be reached and the price become settled again.

The reduction of the duty on monazite imported into the United States, under the terms of the new tariff revision, from



6 to 4 cents per pound, including thorite under the same rating, has opened a small market, at least for foreign monazite and thorite.

No exports of monazite were recorded by the Bureau of Statistics, though the output of one of the companies operating in the Carolinas is shipped to Germany.

There was a production of about 2,000 pounds of zircon, valued at \$250, from the Jones mine, near Zirconia, N. C., operated by M. C. and C. F. Toms. Of the output of zircon at the mine of C. H. Hackney, of Le Harpe, Kans., in the Wichita Mountains, obtained during prospecting, none was placed on the market.

#### MINE RESCUE SERVICE.

A life-saving service for the rescue of miners in time of disaster is about to be inaugurated by the United States Bureau of Mines. Six specially constructed cars, manned by a corps of miners trained in rescue work, and equipped with the latest rescue apparatus and first aid to the injured appliances, will be located in the midst of the great coal districts of the country. These cars will be ready at a moment's notice to proceed to the scene of a disaster.

The cars will each contain eight so-called oxygen helmets, a supply of oxygen in tanks, one dozen safety lamps, one field telephone with 2,000 feet of wire, rescuscitating outfits and a small outfit for use in demonstration.

The first car will be located at Monongahela City, Pa., where the first demonstration of rescue apparatus will be given. Four other cars will make their headquarters at Rock Springs, Wyo., Billings, Mont., Salt Lake City, Utah, and Knoxville, Tenn.

Last year 2,412 men were killed in coal mines and 7,979 injured.

#### MEXICAN CEMENT PLANT.

The "Tolteca" Cement Co. has just completed the most modern plant in Mexico at Tolteca, state of Hidalgo. This factory has been under construction since September, 1909, and has cost upward of 1,000,000 pesos. The company is composed of American capitalists, who have a parent plant at Louisville, Kentucky.

There is not a user of cement in Mexico who will not realize what it means to have a cement manufactured in the country equal in every respect to the best imported article. To begin with, the prices will be materially lower, as the duties and freight rates will be done away with. Unnecessarily high prices have hitherto been a great obstacle to the general use of this material in Mexico.

#### CEMENT FROM BLAST FURNACE SLAG.

[From Consul-General John L. Griffiths, London.]

American inquiries have been made concerning the new cement, similar to Portland, but which has been manufactured in an entirely different manner. A number of letters were addressed by this consulate-general to English architects and engineers, with the result that no one knew anything about the process. The following statement was finally secured from a consulting chemist:

From the nature of the process, namely, the use of blast furnace slag in a perfectly fluid condition, complete combination of the acid and basic oxides—namely, silica, alumina and lime—is insured, and in consequence it might be predicted that the product would be free from any tendency to mechanical unsoundness which not infrequently occurs in cements which contain chemical bodies in an unsaturated or loosely combined condition. Direct and repeated tests show this to be the case. I have no instance on record of a sample of Collos cement which has not proved itself to be absolutely sound. When tested in the

usual way by being made into briquettes, both neat and with sand, it has a high and increasing tensile strength. Tests on concrete blocks show similar good resistance to compressive stresses.

#### SAMPLE 1.—TENSILE TESTS BRIQUETTES, 1 BY 1 INCH SECTION, BOHME HAMMER, 150 STROKES.

[Neat—3 sand : 1 cement.]

7 days. Pounds.	28 days. Pounds.	7 days. Pounds.	28 days. Pounds.
500	675	320	450
45	660	320	425
495	645	320	415
485	615	310	405
465	600	295	405
460	600	250	400
483 1/2a	632 1/2a	302 1/2a	416 2/3a

a Average.

#### COMPRESSION TESTS, 5-INCH CUBES.

[Cubes—1 cement : 5 Thames ballast.]

Crushed.

	Base area. Sq. inch.	Stress. Pounds.	Per square foot. Tons.
7 days.....	{ 25.10 25.10 25.25	{ 16,800 17,940 18,580	{ 43.0 46.0 47.3
28 days.....	{ 25.00 25.00 24.15	{ 50,450 55,200 50,600	{ 129.8 142.0 134.7
3 months.....	{ 24.90 25.00 25.30	{ 47,400 53,060 51,100	{ 122.4 136.5 129.9
6 months.....	{ 25.10 25.00 25.00	{ 62,450 61,600 57,500	{ 160.0 158.5 147.9
12 months.....	{ 25.00 25.00 25.10	{ 63,600 65,700 66,300	{ 163.6 169.0 169.8

#### SAMPLE 2.—TENSILE TESTS BRIQUETTES, 1 BY 1 INCH SECTION, BOHME HAMMER, 150 STROKES.

[Neat—3 sand : 1 cement.]

7 days. Pounds.	28 days. Pounds.	7 days. Pounds.	28 days. Pounds.
585	720	340	430
565	700	325	420
550	685	320	410
550	685	320	410
540	650	305	390
510	640	290	390
550a	75 1/2a	315a	408 1/3a

a Average.

#### COMPRESSION TESTS, 5-INCH CUBES.

[Cubes—1 cement : 5 Thames ballast.]

Crushed.

	Base area. Sq. inches.	Stress. Pounds.	Per square foot. Tons.
7 days.....	{ 25.40 25.10 25.15	{ 18,630 19,410 16,185	{ 47.1 49.7 41.4
28 days.....	{ 25.00 25.05 25.15	{ 40,600 44,910 41,850	{ 104.4 107.6 107.0
3 months.....	{ 25.10 25.20 25.30	{ 52,250 55,700 52,450	{ 133.9 142.1 133.3
6 months.....	{ 25.20 25.20 25.15	{ 67,200 66,300 56,550	{ 171.5 169.2 144.6
12 months.....	{ 25.40 25.40 24.90	{ 64,620 66,780 62,580	{ 163.6 169.1 161.6

I have myself seen the process in operation at Porz and at Harzburg in Germany and have tested numerous samples

made there as well as some prepared at Coltness and by the Conselt Iron Company in this country, the tests in some cases being extended over a year.

The preceding table of tests may be of interest. The figures indicate that the cement in addition to its quality of soundness has ample mechanical strength and possesses all the characteristics of a reliable constructional material.

#### GERMANY'S POTASH DEPOSITS AND MINES.

[From Consul Robert J. Thompson, Hanover.]

Germany is mining over 6,600,000 tons of potash salts yearly. Her exports of this valuable mineral fertilizer already amount in value to \$35,000,000 annually, and by the opening of some 40 more projected mines the output may attain an increase of 100 per cent. within the next decade. The most remarkable feature of the potash industry is that at present Germany holds a world monopoly of this precious soil-rejuvenating product, and it is shown that her mines will continue to yield their wealth for hundreds of years to come, probably long after the exhaustion of her coal mines. Thus her potash mines are coming to be regarded as the unparalleled national treasure of the German economic world.

Many millions of dollars have been lost in the opening of unprofitable mines, speculation, and overproduction. Owing to the temporary disintegration of the great potash trust, or syndicate, the industry was for a short time in a very critical state, but with the renewal of the combination last year, its encouragement by the Prussian Government, and the general improvement of financial conditions it is again making great strides toward a fixed and healthy business condition.

The first kali syndicate (kali is the general term used in Germany for potash) was formed in 1884 in order to regulate the sale of potash and protect the market from overproduction. The present syndicate owns or controls some 60 mines and it is reported will, within a few years, be operating not less than 100. It has 40 branch offices in Germany and abroad and issues extensive and effective propaganda in furthering the sale of its product for agricultural purposes. It has been noted that through its advertising the sales have been increased about \$2,500,000 per year over the average amount sold before this phase of the business was attended to.

Hanover is the recognized center of the potash district, although most of the mines are south and east of here, in the vicinity of the Hartz Mountains. It is claimed that potash deposits are known to exist in Florida, also in China, but if these claims are true, the locations have been held secret and are known only to certain individuals.

In arriving at the present theories respecting the geological formations of the kali beds, or potash salt deposits, of northern Germany, the German scientists go back to the earliest periods of the history of the earth. The millions of years through which the same has passed, since the hardening of its surface crust and the precipitation of its aqueous vapors, are divided by geology into four great groups of formation—the Archean, Paleozoic, Mesozoic, and Cenozoic. These, as well as their subdivisions, are distinguished by their various beds of deposit formed by the gradual washing away of the titanic primeval mountains and slowly cemented into a new stone (sediment stone) through the great pressure of the later deposits.

Calculating from the seventh of these formations, the so-called "permoformation," which up to the present time has been followed by five later formations (trias, jura-limestone, chalk, tertiary, quaternary), and which lies at about the middle age of the geological development, two under-formations—*zechstein* (magnesian limestone) and the lower new red sandstone—have been developed.

The term "*zechstein*" was given to the gray limestone in

the Mansfield copper mines, owing to the fact that to reach the copper, shafts or "*zechen*" were driven through this limestone to the copper layers underneath; thus the denomination came into use for the whole formation found in northwest Germany.

According to Miller and Lyell (1850) and Ochsenius (1878), these limestone deposits originated at a time when high mountains were found in the north and west of northwest Germany, with wide plains stretching themselves to the east, and in what is to-day north and middle Germany, a large, flat inland lake covered the land and was separated from the southern ocean by a barrier dry at ebb tide but under water at high tide. This lake was probably joined to the ocean by a shallow canal, at the bottom of which the concentrated salt solution of the lake was deposited by evaporation. Nevertheless, the salts accumulated through evaporation of the saline water, constantly brought in from the ocean, until anhydrite, sodium chloride, etc., salts not generally easily dissolved were finally separated.

The foregoing theory, known in connection with potash deposits as the barrier theory, was advanced by Professor Ochsenius and elaborated by Everding, and it is now accepted by the Geological Landes-Anstalt at Berlin and many other geologists. On the other hand, other prominent scientists, such as Professor Walther and Professor Erdmann-Halle, maintain the opinion that the salt deposits formed themselves in deserts by the erosion of vast salt mountains, Professor Erdmann claiming that at the time of the *zechstein* formations all middle Europe was covered by a wide inland sea; that this sea evaporated and the salts were separated, and afterwards the saline deposit of the former lake having been redissolved by water, they accumulated again in hollows and subsidences of the earth's crust.

Near Unseburg (Stassfurt, Saxony), where the rock salt has been found 80 meters (meter = 39.37 inches) below the level of the surface of the earth, the whole deposit has been penetrated by boring and found to be 1,170 meters thick. The average thickness of the German potash deposit is therefore estimated to be 1,000 meters.

About 90 per cent. of this deposit consists of layers of rock salt 8-9 centimeters in thickness, between which thin anhydrite layers of 7 millimeters thickness, termed "*year rings*," are embedded.

According to modern science these anhydrite layers crystallized during the hot season, as anhydrite crystallizes only under high temperature. During the cold season, according to the Precht theory, the sodic chloride crystallized. Counting the year rings, it is estimated that the rock-salt deposit required a period of 10,000 years to form.

Owing to the separation of the anhydrite and large quantities of sodic chloride, various salts, such as magnesium salt and potash, accumulated, although in the beginning small quantities only were present. Toward the end of the period the saline solution consisted mostly of sodic chloride, magnesium sulphate, chloride of magnesium, chloride of potassium, and calcium sulphate. As the evaporation progressed, the barrier disappeared, or the canal was closed and the further supply of water discontinued. The calcium sulphate, potash sulphate, and magnesium sulphate crystallized and formed the so-called polyhalite bands which are found to-day and which lay about 60 meters thick above the rock salt which is 600 meters thick. These polyhalite bands form the second salt zone. In the center of this zone is a compound of calcium sulphate, magnesium sulphate, and potash sulphate:  $2\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $2\text{H}_2\text{O}$  (formula supplied by Dr. P. Kriesche).

In the beginning of the crystallization process a mixture of anhydrite, carnallite, and kieserite with large quantities of rock salt were crystallized, later kieserite and carnallite only; this layer is therefore termed the kieserite layer, and the upper part of the layer, containing mostly kieserite and car-

nallite, is known as the carnallite region and forms the main potash deposit of about 25 meters thickness. These crystallizations are not deposited in regular horizontal layers, but followed each other, forming irregular bands dipping and rising and running at tangents.

After this period the potash and magnesium salts, being the easiest to dissolve, were crystallized by evaporation. The light, brilliantly colored mass of salt was covered up eventually by dust, and through this protecting cover and the dry temperature of the desert the potash has remained unaffected by the earthquakes and surface shiftings of later periods. Various depressions were formed in the earth's surface in which water accumulated and salts again crystallized, until finally the layer of dust grew so thick that the rain could not reach the potash lying underneath.

It appears that another great subsidence took place later and another large inland lake appeared which evaporated, leaving new deposits of rock salt, anhydrite, and potash above the original or elder salt. The anhydrite and potash were washed away, but the rock salt remained, and it is through this firm protection that at least one layer of the precious potash salt, in spite of its illusiveness, has been preserved to the present age. Through the shiftings of the ground and earthquakes, the deposits which at first lay in level zones were torn asunder and thrown into a confused mass; they were partly washed away and crystallized again in distant places.

According to the indicated shiftings of the earth's crust there are three different kinds or deposits of potash: First, the mother salt, or that which did not change after its original crystallization; second, the descendant salts, or those which crystallized themselves directly out of the former in consequence of ground-shiftings; third, posthumous salts, or those which formed still later in consequence of earthquakes, floods, etc.

At first the potash crystallized as double-salt carnallite; this is called by Everding the main salt. It is found everywhere where potash exists and forms the base, so to speak, of all potash salts. When floods occurred, the first thing washed away was the chloride of magnesium, leaving a mixture of carnallite, kieserite and rock salt, which changed into a mixture of chloride of potassium, kieserite, and rock salt. This mixture is called hard salt and was formed, as shown by experiments made by van't Hoff, at a temperature of 73° C.

Through a falling temperature and the disappearance of chloride of magnesium, caused by floods and the formation of a solution of magnesium sulphate and potassium sulphate, another double salt evolved, namely, kainite or chloride of potassium-magnesium sulphate ( $\text{KClMgSO}_4 \cdot \text{H}_2\text{O}$ ).

Everding, one of the chief authorities on this subject, is of the opinion that, to form kainite, the floods must have been in effect for a long period of time. According to his theory the chloride of magnesium was washed away, the kieserite then changed into sulphate of magnesium and this sulphate, in combination with chloride of potassium, afterwards changed into the double-salt kainite.

Through long-continued floods the kieserite, or sulphate of magnesium, was also washed away and a mixture of sylvine—another denomination for chloride of potassium—and rock salt was crystallized. This mixture is called sylvinit.

Beside the various kinds of potash referred to there are a number of other salts, though rarely to be found, such as schönit, langbeinit, krugit, etc.

Potash was first found at Stassfurt near Magdeburg. The formation of the potash deposits at this place was such as to show very clearly the different layers. Since the days of the old Carolingian kings salt mines and saline springs have been commercially operated here. In the Middle Ages deep wells were made and yielded their owners a considerable profit by the sale of the salt recovered. In 1797 the Prussian Govern-

ment bought the Stassfurt saline works, shafts were bored, and rock salt was found. In 1856 a new colored rock salt was found, an unknown mineral, tasting bitter; the value being unknown it was thrown away as waste salt. Afterwards chemists discovered that the so-called waste salts contained magnesium and potash, and thereupon the chemical industries became interested. Successful experiments were made, and very soon a flourishing chemical industry sprang up at Stassfurt. The original rock salt was neglected, there being a great demand by the chemical works as well as the agricultural interests for potash.

The potash deposits at Stassfurt stretch very regularly in the form of a saddle of 20 kilometers length, with layers extending from this saddle at both sides. In mining, potash is not loosened from above but from below with blasting work and tunnels running diagonally upward. The ore is thrown into 300 to 1,000 meters deep shafts and from the bottom of the mine hauled up through the main shaft.

On being elevated to the mouth of the mine the potash is despatched directly to the mill, where it is ground and sold as manure salt, or to chemical plants for further reduction. The majority of the potash mines are therefore combined with a chemical factory (chloride of potassium plant), and nearly all have railway connections.

## OFFICIAL REGULATIONS AND RULINGS.

### FOOD INSPECTION DECISION NO. 127.

The following decision of the Attorney-General in regard to the labeling of whiskey is hereby promulgated as Food Inspection Decision No. 127.

WILLIS L. MOORE,

*Acting Secretary of Agriculture.*

WASHINGTON, D. C., October 26, 1910.

DEPARTMENT OF JUSTICE,  
WASHINGTON, October 19, 1910.

The honorable the SECRETARY OF AGRICULTURE.

SIR: I have received your letter of July 28, 1910, in which you submit to me the following question of law for my opinion:

Is "Canadian Club whiskey" such a distinctive name, under the provisions of Section 8, paragraphs 10 and 11, of the Food and Drugs act of June 30, 1906 (34 Stat., 768), as to relieve a mixture of two separate and distinct distillates of grain from the requirement of being labeled "A blend of whiskeys," under Section 8, paragraph 12, of the same act?

Your letter informs me that—

"Canadian Club whiskey" is a mixture of grain distillates, duly aged after mixing, without further admixture, and reaches the consumer at 90° proof. It is a particular kind and brand of whiskeys made by Hiram Walker & Sons (Limited), at Walkerville, Ontario, and is now and has been for years known and sold under the name "Canadian Club whiskey." It is known by that name and no other to the trade and consumers in the United States and other countries, and no other whiskey is known by that name. "The Department of Agriculture," you advise me, "claims that the product is required to be labeled 'a blend of whiskeys,' under the law as interpreted in Food Inspection Decision 113. The distillers contend that 'Canadian Club whiskey,' under Section 8 of the Food and Drugs act, is such a distinctive name as is there described, and therefore that the product is not required to be labeled as a blend."

By arrangement between your Department and Messrs. Hiram Walker & Sons (Limited) briefs were submitted to me by the Solicitor of your Department and the counsel of Messrs. Hiram Walker & Sons, respectively, in support of their respec-



tive contentions; and I have also had the assistance of oral argument by such Solicitor and counsel.

\* \* \* \* \*

The brief of the Solicitor of the Department of Agriculture contends that the distinctive name under which a mixture or compound may be sold must, in its entirety, be purely arbitrary or fanciful, and must not contain the name of the component elements of the compound. A mixture of wheat and barley, he concedes, might be sold as "Force" or "Vita" without stating of what elements it was composed, but a mixture of two kinds of barley could not be sold as "Melrose barley" without stating that it was a "blend of barleys." It seems to me that such a construction of the term "distinctive name" is not only unwarranted, but undesirable. The two main purposes which the pure-food law was designed to accomplish are first, to prevent the sale of adulterated foods, and, second, to prevent deception being practiced on the public. It would seem to me that the latter purpose is more apt to be secured by permitting the sale of a product under its own name, qualified by some distinguishing characterization, than by requiring it to be masked in an anonymity which would give no clue to any of its component elements.

But, without entering into an analyses of the many decisions cited in the briefs of the respective parties, or further pursuing a discussion of the question, it appears to me clear that the name "Canadian Club whiskey" is a distinctive name, so arbitrary and so fanciful as to clearly distinguish it from all other kinds of whiskey or other things, and a name which, by common use, has come to mean a substance clearly distinguishable by the public from everything else. (See United States v. 300 Cases of Mapleine, per Sanborn, D. J.; Notice of Judgment 163, Food and Drugs Act, p. 3.)

In my opinion, therefore, it is not necessary that the label under which "Canadian Club whiskey" is sold shall state that it is "a blend of whiskeys."

I have the honor to be, respectfully,

GEO. W. WICKERSHAM,  
Attorney-General.

#### FOOD INSPECTION DECISION NO. 128.

##### *Sago and Tapioca.*

It has come to the attention of the Board of Food and Drug Inspection that there exists among the trade in various parts of the United States a very general misunderstanding with respect to sago and small pearl tapioca. Sago is prepared from the starch obtained from the pith found in the stem of several species of palm trees, natives of the East Indies, and tapioca is prepared by heating in a moist state the starch made from the root of the cassava or tapioca plant, which is indigenous to

certain South American countries. Both products ordinarily reach the consumer in granulated form and are designated as "pearl sago" and "pearl tapioca," respectively. While "pearl sago" and "pearl tapioca" are separate and distinct articles of commerce, each resembles the other closely in appearance, and fine pearl tapioca frequently has been labeled and sold as sago.

Under the Food and Drugs Act of June 30, 1906, articles of food are misbranded if the labels or packages contain statements which are false or misleading, or if particular articles are imitations of or offered for sale under the distinctive names of other articles. In the opinion of the Board the name "sago," or "pearl sago," without qualification, means the product obtained from the pith of East Indian palm trees, and starch products of different origin will be held to be misbranded under the act if labeled or offered for sale as "sago," "pearl sago," etc. The prepared starch product derived from the root of the cassava plant is tapioca, and should be sold and labeled as such.

There is also on the market an imitation sago made from potato starch. Imitation food products are misbranded under the act unless they are labeled so as to indicate plainly that they are imitation products and unless the word "imitation" is also plainly stated on the packages in which imitation products are offered for sale. Potato or other starch prepared to resemble pearl sago, therefore, should be labeled, for example, "Imitation sago. Made from potato starch," the words "Imitation" and "Made from potato starch" being declared as plainly and conspicuously as the word "sago." The word "Imitation" must appear on the label, but an equivalent expression may be substituted for "Made from potato starch," which will indicate unmistakably that the product is not made from the pith of East Indian palm trees, but is derived from a different source.

H. W. WILEY,  
F. L. DUNLAP,  
GEO. P. MCCABE,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,  
*Secretary of Agriculture,*

WASHINGTON, D. C., October 31, 1910.

#### CORRECTION.

The title of my paper (THIS JOURNAL, 2, 385) should read "A Comparison of Bolling's and Harding's Modification of Drehschmidt's Method for Determining Sulphur in Illuminating Gas." In the last table the word grains should be substituted for grams.

DR. E. P. HARDING.

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